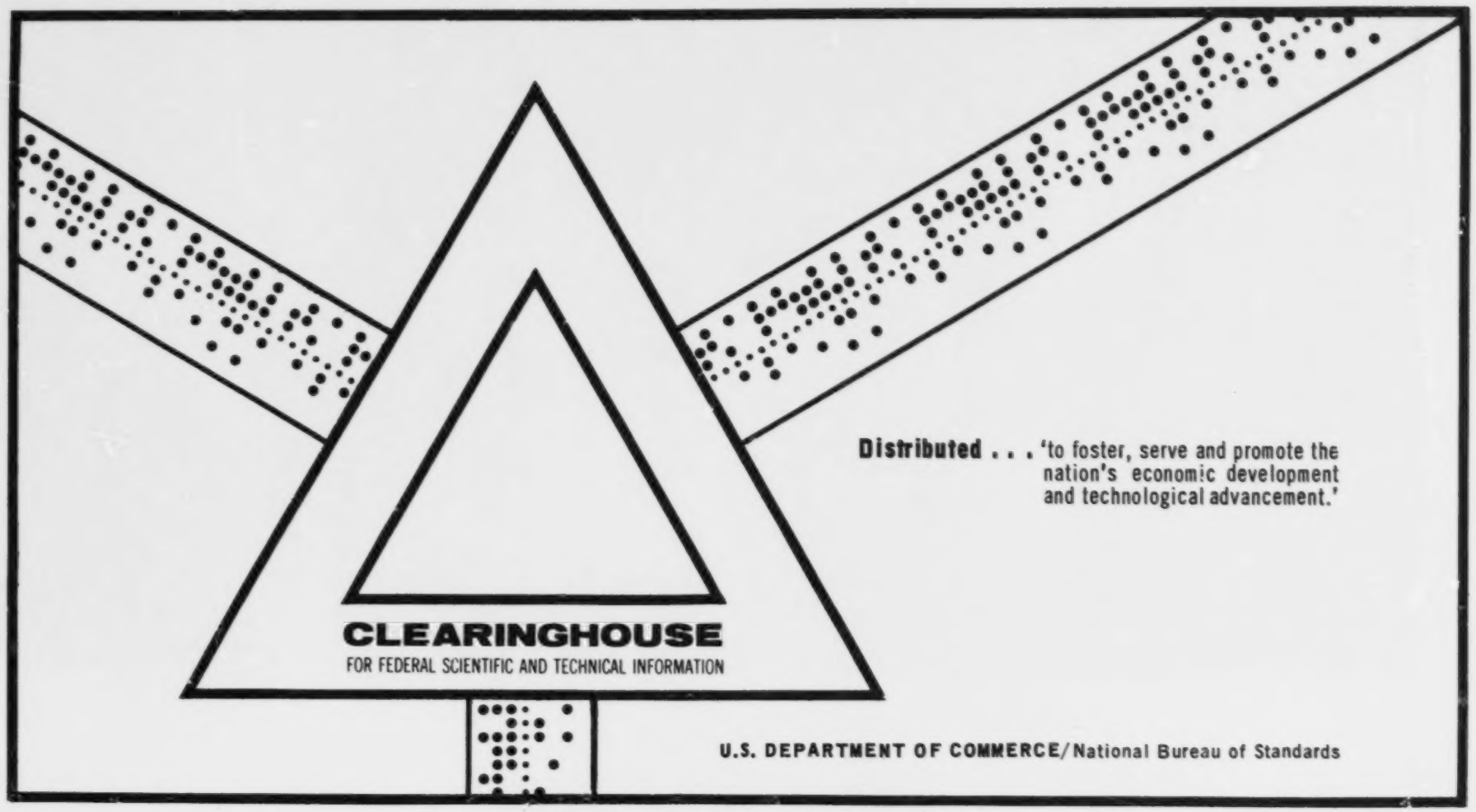
PB 189 160

FOAM SEPARATION OF KRAFT PULPING WASTES

Georgia Kraft Company
Rome, Georgia

October 1969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Foam Separation of Kraft Pulping Wastes

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FOAM SEPARATION OF KRAFT PULPING WASTES

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

DEPARTMENT OF THE INTERIOR

BY

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Research and Development Center
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ABSTRACT

Laboratory studies of foam separation were conducted to determine the feasibility of this process for reducing B.O.D., solids content, and foaming tendency of clarified kraft mill effluent. Since kraft pulping wastes have a natural tendency to foam, it was expected that the foaming process, which has been found to be useful in treating domestic wastes, might have applications in treatment of these effluents.

Both continuous flow and batch experiments were conducted, and liquid and foam heights, liquid feed rates, air sparging rates, and temperature were varied over wide ranges.

The B.O.D. reduction in the treated liquid was disappointingly small, averaging less than 5 per cent, and the B.O.D. enrichment in the foam phase was in most cases less than 1.5 times that of the feed. Solids removal was correspondingly low.

Foaming tendency, however, was significantly reduced by the intentional foaming process with reductions of 40 to 60 per cent in this variable being obtained. The reduction in foaming tendency was a strong function of gas-to-liquid ratio with the most effective operating range being between 1.0 and 1.5 SCFM/gallon.

The experimental results suggest that the reductions in B.O.D. and foaming tendency were related to the separation of the tall oil components of the waste. These components were concentrated in the foam fraction, but they accounted for a maximum of only 10 to 12 per cent of the B.O.D. of the raw feed. Apparently the remaining B.O.D.-producing materials were not surface active and did not attach themselves to the surface-active components.

The cost of using a foam process on kraft mill wastes is estimated to be four to five cents per 1000 gallons of feed; this cost is exclusive of further processing of the concentrated foamate. Based on control of foaming tendency alone, the process would be unattractive from a cost standpoint.

This report was submitted in fulfillment of Grant No. WPRD 117-01-68 between the Federal Water Pollution Control Administration and Georgia Kraft Company.

Key Words: Foam separation, pulping wastes, B.O.D. removal, tall oil removal, foaming reduction, solids removal, treatment costs.

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Foam Separation of Kraft Pulping Wastes

I. SUMMARY

Foam separation has been found useful to biologists, chemists, and engineers as a means of separating and concentrating materials in aqueous suspensions and solutions. Dissolved substances collect at a gas-liquid interface in accordance with their surface activity, and the more active ones can be separated from a solution by foaming and can be concentrated by foam drainage. Less active substances must be attached to a more active substance if they, too, are to be removed. Separations have been achieved for a great variety of substances, including proteins, enzymes, fatty acids, detergents, anions, cations, phenols, colloidally suspended particulates, and biologically active components of domestic sewage. Studies of these separations have ranged from mere scientific inquiry to searches for practical applications.

Since kraft pulping wastes contain natural surface-active materials, it would appear that the dissolved and suspended components in these wastes could likewise be removed by foaming. Previous studies have indicated that foaming may be effective in treating kraft mill wastes, but there were essentially no data exploiting the potential of the process. A proposal, therefore, was submitted to the Federal Water Pollution Control Administration to explore the feasibility of the method. The ultimate objective was to define an optimum process design for removing components of high B.O.D. from kraft mill streams. Specific objectives were to study the process as it was affected by equipment design, gas and liquid flow rates, effluent composition, and temperature.

The study was carried out in a cylindrical column in which liquid descended countercurrently against rising bubbles of air which generated the foam. The foam product was mechanically broken and discharged from the column as a liquid. Part of the liquid was returned to the column as reflux. Liquid feed entered through the side of the column and treated liquid was removed from the bottom of the column. The temperature of the process was adjusted by heating the feed stream.

A series of steady state flow experiments was conducted to study the effects of major variables. Liquid column height, liquid feed rate, and gas sparging rate were considered the three basic operating variables and were investigated in a 3^3 factorial experiment. The experimental plan was to locate the optimum combination of these three variables and then investigate all others at this condition; interactions would be clarified if necessary. The additional variables included sparger porosity, temperature, feed location, foam height, waste stream properties, and pH.

In addition to the flow experiments, batch experiments were performed to ascertain the ultimate treatment attainable by foaming and to study the effects of the individual operating variables more precisely than was possible in the flow experiments.

The tests performed on the various streams included B.O.D.$_5$, C.O.D., total solids, total organic solids, tall oil, alkalinity, foaming tendency, and pH. The tests were performed on the feed, treated liquid, and foamed product streams. Experimental results showed foaming tendency reduction to be the most significant change produced in the mill effluent by foam treatment. A reduction of at least 40 per cent was always obtained, and under favorable conditions as much as 60 per cent was found. Foaming tendency reduction was a function primarily of the gas-to-liquid ratio, and the most effective operating range was between 1.0 and 1.5 SCFM/gal with a reduction of 50 per cent.

The amount of foam produced by air sparging was also a significantly varying function of the gas-to-liquid ratio and of the reflux returned to the column. With no reflux, a certain minimum amount of sparging air could be introduced to the foam column without producing any foam product at all. Above this critical air-to-liquid ratio, the foam production varied linearly with air sparging to the maximum condition studied where 35 per cent of the feed was converted to foam. When part of the foamed product was returned to the column, the rate of foam production was greatly increased. At a reflux of four (ratio of returned liquid to product liquid) the foam production was over 90 per cent of the feed rate, and at greater reflux values the foam production increased gradually and asymptotically approached about 97 per cent of the feed rate at infinite reflux (all foam product returned).

The reduction of B.O.D. was found to be surprisingly small in all of these studies. Throughout the course of the experimental work, the B.O.D. concentration in the feed stream was reduced no more than 5 per cent, and the B.O.D. enrichment in the foam stream was no more than 1.5 times that of the feed. No combination of physical operational variables produced any significant improvement in treatment.

The experimental results suggested that the removal of B.O.D. is related to the separation of tall oil by the foaming process. The tall oil content was approximately 6 per cent of the total organic content, and this amount was calculated to constitute approximately 12 per cent of the total B.O.D. Since only 50 per cent of the tall oil at the most was removed by foaming in the flow experiments, the maximum B.O.D. concentration reduction produced by the foaming process as practiced was estimated to be around 6 per cent at best. Apparently, the remaining B.O.D.-producing materials were not surface active, did not attach themselves to the surface of the surface-active components, and were not removed.

The C.O.D. concentration was reduced around 6 to 8 per cent and, like B.O.D., corresponded closely to the amount of tall oil removed from the effluent stream.

The experimental findings suggested that foam treatment might possibly be used for reducing foaming tendency of the mill effluent to combat the formation of foam flocs or "snow" on the aeration ponds. The cost for such treatment was estimated to be four to five cents per 1,000 gallons. With the present estimate, the cost of treating effluent by foaming would be more than by using chemical defoamers, and additional costs would be incurred in the disposal of the foamate product. The latter cost could be considerable if the amount of foamate is not reduced to a minimum and if the process is not operated as near infinite reflux as possible. Foam separation treatment, on the other hand, would likely produce consistent and positive control of the adverse foaming conditions frequently occurring in the Rome mill treatment plant.

Operation of the foam separation process in a series of columns was considered as a method for increasing the removal of B.O.D. Calculations, however, indicated that the process was not adaptable to multistate operation since the number of columns required to produce practical results would not be economical.

While foam treatment in this study was definitely limited, the process could still have potential if chemical additives were found to increase the surface activity of non-foamable compounds in the liquid or to attach these compounds to others which are surface active. If foam separation is ever to be effective on kraft mill liquids for removing organic constituents, a program of fundamental research should be performed to study the effects of potential chemical additives.

II. CONCLUSIONS

A. In the steady flow experiments the B.O.D. (ppm) was reduced no more than 5 per cent in the primary clarifier effluent, and the B.O.D. enrichment in the foam stream was no more than 1.5 times the B.O.D. in the feed. The maximum B.O.D. that could be separated from primary clarifier effluent with extended treatment in the batch process was up to 10 to 15 per cent. No combination of physical operational variables was found capable of improving the B.O.D. removal.

B. The reduction of B.O.D. and C.O.D. appeared to be related to the removal of tall oil which was the only organic constituent specifically investigated. The tall oil amounted to about 5 to 6 per cent of the total organic content, and calculations indicated that it could exert a maximum of 12 per cent of the B.O.D. of the feed. Since analytical measurements indicated that up to approximately one-half of the tall oil was removed, the reductions in B.O.D. and C.O.D. were estimated to be around 6 per cent, which compared favorably with the maximum removal of 5 per cent found by foaming experiments.

C. Apparently the major B.O.D.-producing materials are not surface active and do not attach themselves to those materials that are. Measurements showed that the total solids and the total organic content other than tall oil were practically unchanged by foaming.

D. Foam separation could reduce foaming tendency up to 60 per cent, and this reduction was probably related to about the same percentage of tall oil removal.

E. Foam separation could possibly be used to control foaming tendency. The cost of such treatment would be four to five cents per 1,000 gallons, exclusive of the cost for handling the foamed product. Further development work might show a more favorable cost estimate. The foamate disposal cost could be minimized by operating as near infinite reflux as possible.

III. RECOMMENDATIONS

A. Foam separation as it is presently understood is not recommended for removing B.O.D. from kraft mill effluent.

B. Foam separation could be considered further as a potential process for reducing foaming tendency of kraft mill effluent.

C. Future research should be conducted to determine suitable additives for achieving the removal of non-surface-active organic compounds in kraft mill effluent.

IV. INTRODUCTION

A. Background Information

1. Theory and Fundamental Studies

Certain materials dissolved in aqueous systems have a tendency to concentrate at a gas-liquid interface such as found in the liquid films surrounding gas bubbles in foams. The mechanism has been useful to biologists, chemists, and engineers as a means of treating aqueous solutions and suspensions for removing numerous materials, including proteins, enzymes, fatty acids, detergents, anions, cations, phenols, colloidally suspended particulates, and biologically active components of domestic sewage, to name some of the more notable results. In special cases, surface-inactive and weakly surface-active materials (those that do not collect at an interface) have been removed by adding foaming agents which attach to the material to be separated. Foaming is usually produced by sparging air through the liquid solutions.

The fundamentals of foam separation and foam fractionation have been investigated in depth for quite a number of systems, and these processes, as currently understood, have been recently summarized in excellent reviews by R. Lemlich *(1 & 2)*, R. B. Grieves, et. al. *(3)*, C. A. Brunner and D. G. Stephan *(4)* and J. L. Rose and J. F. Sebald *(5)*. The more salient features of these reviews, together with supporting information from other pertinent references, served as the background for the study herein reported. For more detailed study, the referenced articles are recommended.

The collection of a solute at a gas-liquid interface, under equilibrium conditions, is described by the Gibbs equation *(6)*

$$d\gamma_i = -RT\sum\Gamma_i \, d(\ln a_i) \qquad (1)$$

In this relationship, γ is the surface tension of the i^{th} component and a_i is its activity; R is the gas constant, T is the absolute temperature, and Γ_i is the "surface excess", which is essentially the concentration of the component i at the interface in units of mass per unit area (e.g., grams per square centimeter). The equation can be used to predict the concentration of a surface-active material at an interface provided sufficient data are available; such, however, is usually not the case for most systems of interest because of their extreme com-

plexity. Experience teaches that the variation of the solute concentration at the surface is linearly related to the bulk concentration in very dilute solutions and tends to approach a constant value in more concentrated solutions *(1)*. Materials present in trace quantities follow the linear portion of the curve, very dilute metallic ions being an example, while major surfactants in a foam usually involve the constant portion of the surface-to-bulk liquid concentration relationship. Although the theoretical evaluation of the relationship might be difficult or even impossible, it can be derived experimentally and used in theoretical analysis of foam fractionation *(1)*.

If at least one surface-active material is present, other materials which may be surface inactive can, under carefully controlled conditions, also be removed from solution *(7)*. In these cases the surface-inactive component must be united to the surface-active material by some means. Successful interactions have been achieved with chemical processes such as chelation and hydrogen bonding and physical actions, including ionic attraction, electrostatic attraction, and physical adsorption. Many surface-inactive materials, including colloidal particulates *(8)*, bacteria *(9 & 10)*, metallic ions *(11 & 12)*, proteins *(13)*, phenols *(14)*, and selected organic compounds *(15)* have been separated from aqueous solutions with foaming techniques.

As the surface-active properties of a dissolved substance are responsible for its initial surface concentration buildup, foam drainage is an equally dominant factor in increasing the concentration further. Bubbles emerging from a liquid entrain more liquid than can remain with them; and, as they rise, liquid drains due to gravity and pressure differences, leaving surface-active materials behind to become more concentrated. These materials compete in the concentration process according to their level of surface activity and, as drained liquid flows downward between bubbles, tend to concentrate in different parts of the foam with the more surface active toward the top and the less surface active toward the bottom. The resulting concentration and fractionation in foam drainage can have practical significance *(16)*.

The separation of materials from a liquid solution by intentional foaming and the fractionation of these materials have been thought to be useful in a continuous process with properly controlled liquid and air flow rates and product refluxing. Several fundamental analyses of the process have therefore been made *(3, 16, & 17)*. In general, it is concluded that practical applications are possible and that the operation is affected by the gas-to-liquid

ratio, residence time of the foam and the liquid in the process, the amount of reflux and its position, feed position, bubble size, and temperature. There is also strong evidence in one or more of the cited references of the following:

a. Equilibrium at the gas-liquid interface in the liquid pool is rapidly achieved and longer residence times do not influence the separation *(3)*.

b. The liquid behaves as a single stage, not appreciably affected by height if the air sparger is at least one foot submerged *(1, 3, & 17)*.

c. Foam is a good column packing and serves as a medium for foam fractionation by liquid drainage over the bubble surfaces, provided the liquid content is approximately 10 per cent or less *(1)*.

d. Refluxing part of the foamed product aids fractionation in a foam provided the liquid content of the foam does not become too great *(1)*.

e. A foam column can be operated as an enricher, a stripper, or both *(3)*.

f. Foam drainage produces enrichment and fractionation *(16 & 18)*.

g. The overall separation in a foaming process is governed by the separation occurring in the regions adjacent to the foam-liquid solution interface *(16)*.

h. Little is known about multicomponent effects *(2)*.

2. Applications in Waste Treatment

Applied research has been conducted on the pilot plant scale where detergents were added to foam treat domestic wastes *(4, 5, & 19)*. In these experiments, very favorable treatment was obtained. Removals of C.O.D. as high as 42 per cent and organic content removals as high as 65 to 75 per cent were reported. The costs were projected to be three to five cents per 1000 gallons for most operations. A very large plant (100 mgd) was estimated to operate for approximately 1.5 cents per 1000 gallons.

3. Applications Other than Waste Treatment

Foaming is sometimes associated with flotation, which has been widely employed in the mining and metallurgical in-

dustries *(2)* and more recently in studies of water clarification *(20)* and of domestic waste treatment *(21)*. Flotation is a physical process involving particles larger than colloids that become attached to rising bubbles. While surface-active agents may be used to enhance the attraction of particulates to bubbles, the process generally is not one for concentrating dissolved chemicals *(1)*. Certain colloids, however, are an exception and can collect dissolved materials *(8 & 11)*.

4. Treatment of Kraft Mill Streams

Although a considerable amount of research has been conducted on foam separation processes, very little attention has been given to the foam treatment of kraft mill liquids which foam naturally and profusely due to fatty acid and resin acid soaps produced from the pulping of southern soft woods *(5)*. The National Council of the Paper Industry for Air and Stream Improvement considered foam separation in a study of color removal but abandoned it in favor of other processes *(22)*. The use of foam separation as a means of reducing B.O.D., however, was recommended for further study. Harding *(18)* studied foaming as it pertained to black liquor oxidation and foam fractionation of tall oil. He found that tall oil enrichment could be achieved. Foaming in black liquor oxidation has been recommended as a means of increasing tall oil yield *(23)*. Finally, the profuse foaming in kraft mill effluent treatment plants has caused unending concern, and numerous additives have been developed to combat the formation of uncontrollable amounts of foam, but no attempt has been made to use these foams as a method of removing the troublesome foam-making materials.

B. Proposal to Investigate Foam Treatment of Kraft Mill Wastes

If foam separation can be used to treat domestic sewage and other aforementioned solutions of organic materials, some with additives of a suitable surfactant, it would appear that naturally foaming kraft mill wastes could likewise be treated. Such a process, if effective, could be very useful in the future when increased urbanization and industrialization place greater demands on waste treatment facilities to preserve the water resources of the nation. Combinations of several treatment processes currently available (activated sludge, trickling filters, electrodialysis, ion exchange, foaming freezing, etc.) will undoubtedly be required to satisfy these needs of the future. Each new treatment process which is shown to be technically and economically feasible gives the design of waste treatment plants added flexibility and new possibili-

ties for decreased treatment costs. Foam separation is one of the newer techniques which could offer promise for treating industrial wastes.

Since there were essentially no data available on the treatment of kraft mill effluent by foaming, a proposal was submitted to the Federal Water Pollution Control Administration to explore the feasibility of the method. The study was prefaced on the assumption that foaming would treat kraft mill wastes, and the experimental program was designed to yield data on the degree of treatment which could be expected over a wide range of equipment design and operating conditions. The data were to provide a basis for estimating the technical and economic feasibility of the process and for scaling a laboratory apparatus into a small commercial treatment facility. The overall objective was to define an optimum process design for removing components of high B.O.D. from kraft mill streams. The specific objectives for the study were:

1. To study the process as it was affected by

    a. Foaming equipment design
    b. Residence time of liquid and foamate
    c. Effluent flow rate
    d. Air to effluent flow ratio
    e. Effluent composition
    f. Temperature

2. To evaluate methods of breaking and disposing of the foam generated.

3. To determine design data for a commercial or semi-commercial foam separation installation.

4. To estimate the cost of treating kraft mill effluent by foaming techniques.

As the study progressed, it was found that foaming was limited in its potential to remove B.O.D. and that kraft mill effluent was not treatable to a practical level in its natural state and without supplementary chemical aids. The objectives, therefore, were amended but were kept in the original framework of the proposal. The amendments were to:

1. Limit the equipment design to cylindrical columns.

2. Study only fundamental problems and not attempt the development of commercial design data.

3. Provide only very rough estimates of the cost of treating kraft mill effluents by foaming techniques.

V. EXPERIMENTAL METHODS

A. Equipment

The foam separation experiments were conducted in a cylindrical column constructed as schematically represented in Figure 1 and as shown pictorially in Figure 2. The design was principally one in which liquid feed descended countercurrently against rising bubbles of air. The column, 6.5 inches in diameter, was made up of 24-inch flanged sections used as needed to vary the column height from 2 to 12 feet. It contained the liquid pool and the foam phase above it. The height of the liquid was controlled by the hydrostatic leg mounted alongside the column. Some flow was allowed to pass through the hydrostatic leg to assure its remaining full. Liquid feed entered through a circular flow diffuser mounted through the side of one section; changing the position of the section varied the feed position in the column. A second diffuser was used for adding reflux at positions other than at the feed level. Air introduced through the sparger at the bottom of the column generated the foam phase on rising through the liquid pool. Treated liquid discharged from the base of the column, and foamed product rose through the top. The air sparger was a standard fritted glass filter available from most laboratory equipment supply houses. Three porosities, having average pore sizes of 25-50, 70-100, and 145-175 microns, were used. The effective sparger diameter was 4 inches, and the assembly diameter was 5-1/4 inches. These dimensions provided uniform coverage of sparging air across the column and allowed a sufficient annular cross section for the down flow of treated liquid. The upper face of the sparger was approximately 2 inches from the column base.

The foam collector was a cubical chamber mounted above the column. A squirrel cage air blower drew the foam from the column and collapsed it. A perforated plate was positioned atop the column to stabilize the foam withdrawal.

Input flow rates were measured with rotameters. The feed was variable from 0.1 gpm to 2.0 gpm, and the sparging air rate was variable from 0.1 cfm to 1.3 cfm. Reflux, product, and treated liquid flows were measured by timed sample collections.

After leaving the foam breaker, the collapsed foamate was divided into a reflux and a product stream. The reflux was usually returned to the column with the feed stream, although it could be added separately. The reflux was necessary to control the amount of product since the usually profuse foaming of kraft mill effluent would remove more liquid as foam than could ever be handled in a practical operation. Also, it was thought that refluxing might induce fractionation of the surface-active materials in the foam column.

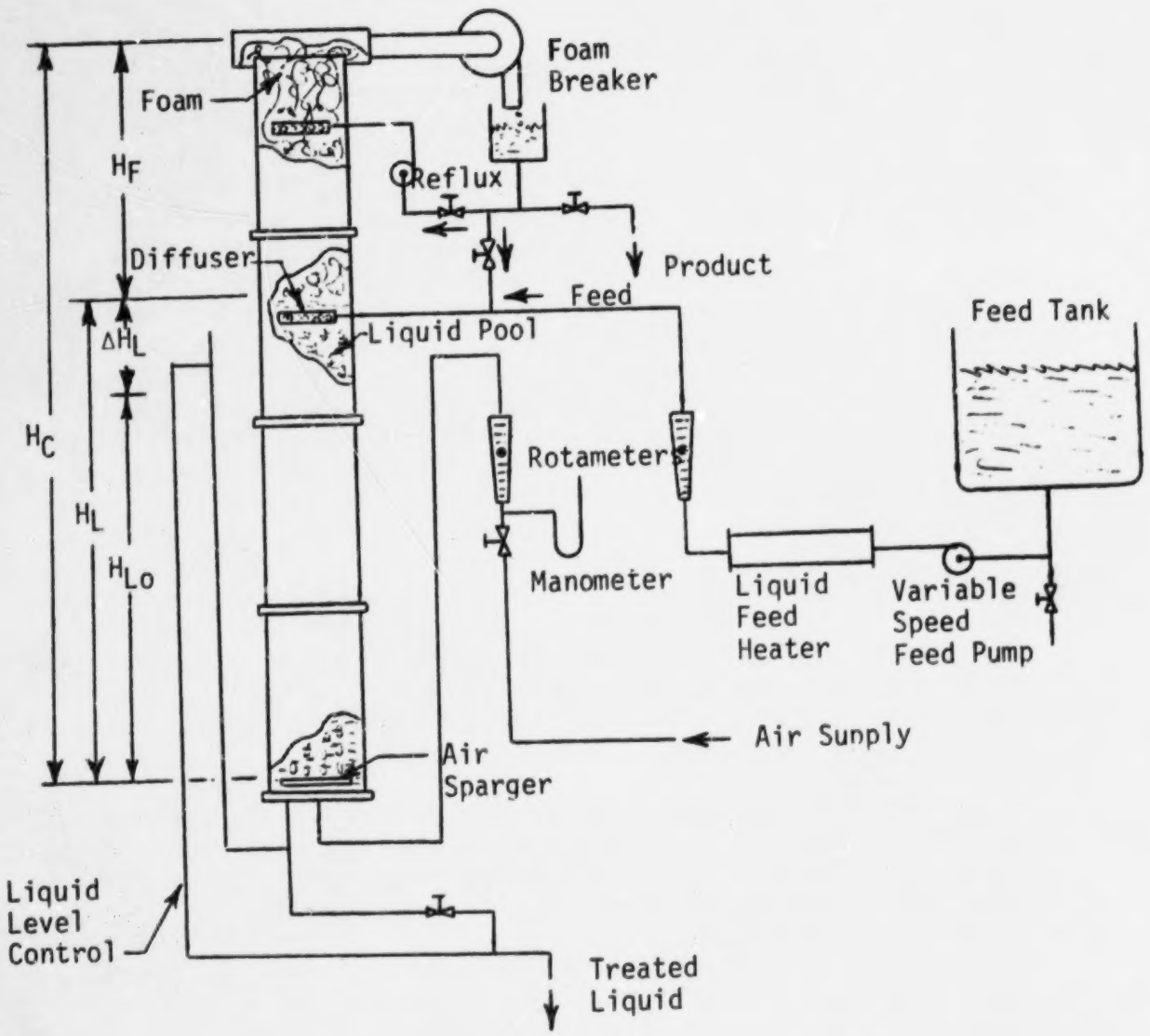

FIGURE 1: SCHEMATIC DIAGRAM OF FOAM SEPARATION APPARATUS

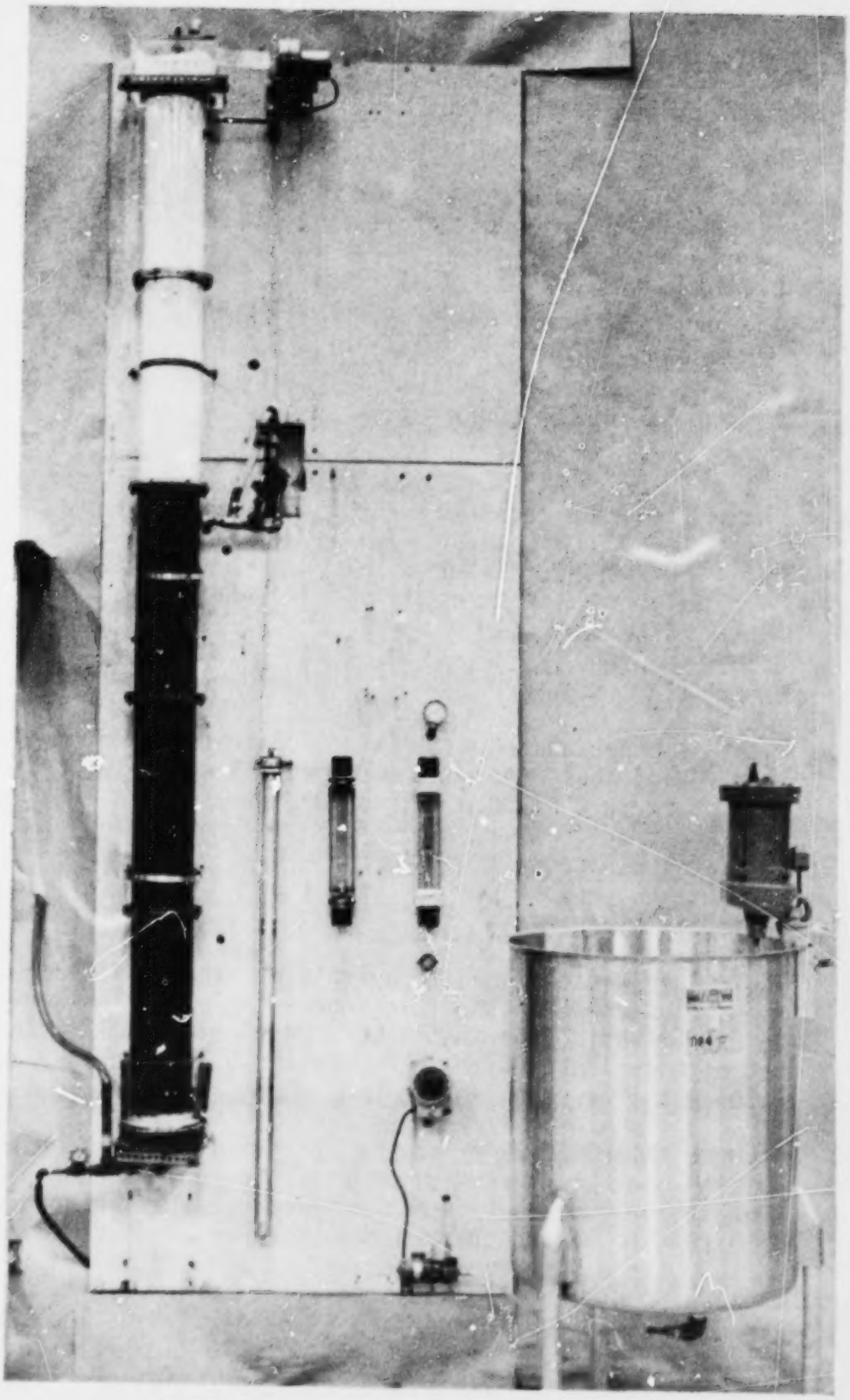

FIGURE 2: FOAM SEPARATION APPARATUS

Nomenclature for column dimensions and operational variables were:

H_C = Total column height, feet

H_F = Foam height, feet

H_{Lo} = Liquid height without air flow, feet

H_L = Liquid height with air flow, feet

$\Delta H_L = H_L - H_{Lo}$, feet

F = Feed flow rate, GPM

G = Air flow rate, CFM

B = Bottom flow rate (bottoms meaning treated effluent), GPM

T = Tops flow rate (tops meaning total collapsed foam), GPM

P = Product flow rate, GPM

R = Reflux flow rate, GPM

X_F, X_B, X_T = Undesignated material concentration, or property of tops, feed and bottoms, respectively, relating to B.O.D., C.O.D., solids, etc.

B. Steady State Operation

1. Factorial Experiments

The column was designed to operate at steady flow conditions, and the effects of its operating variables were to be determined. Experiments were begun with a 3^3 factorial set of experiments with the variables being liquid flow rate, gas flow rate, and column height.

The raw material was primary clarifier effluent from the pulping operations of Georgia Kraft Company at Rome, Georgia; test samples from the primary clarifier were withdrawn as needed over an extended period of time and varied with day-to-day operation. The factorial design was confounded to eliminate the first order effects of the changes in feed properties (Appendix I-A). The three levels of operation were at: (1) liquid flow rates of 0.2, 0.6, and 1.0 gal/min, (2) air flow rates of 0.13, 0.39, and 0.78 SCFM, and (3) column heights of 2, 4, and 8 feet.

These conditions gave: (1) gas-to-liquid flow ratios from 0.13 to 3.9 SCF/gal, (2) gas flux rates from 0.07 to 3.9 SCFM/ft^2, (3) liquid flux rates from 1.0 to 5 GPM/ft^2, and (4) liquid residence times from 3.4 to 69 min. These levels were selected to span the ranges expected to be of commercial importance. Work by Rose and Sebald *(5)* suggested these levels would cover the range of practical value. It was intended that the optimum operating condition for the liquid feed flux, gas feed flux, and column height would be derived from the factorial experiment. For the resulting optimum, the effect of other pertinent design variables would be investigated.

2. Effects of Other Design Features

Other features of the process which were thought to be pertinent were investigated as follows:

a. Temperature Effects

A tube and shell, steam heated heat exchanger was provided to control the feed temperature and determine the effects of this variable. Temperatures at three levels, 75-85°F, 110-115°F, and 135-145°F, were investigated.

b. Feed and Reflux Location

The effects of the different positions of these streams were investigated in experiments with a liquid column of 4 feet and a foam column of 8 feet with:

(1) Both the feed and reflux at the liquid surface.

(2) The feed at the liquid surface and the reflux at the top of the foam column.

(3) The feed 4 feet above the liquid surface and the reflux at the top of the foam column.

(4) Both the feed and the reflux 4 feet above the liquid surface.

c. Sparger Porosity

The effects of sparger porosity were studied with spargers having average pore sizes of (1) 25-50 μ diameter, (2) 70-100 μ diameter, and (3) 145-175 μ diameter.

Each of the design features were separately investigated, and due to the results as they became known, it was not necessary to study the interactions of these variables among themselves or with the factorial experiment results.

C. Batch Operation

Batch operation of the foam column gave a supplementary means of evaluating the potential of removing B.O.D. from the feed liquid in terms of a characteristic enrichment factor and in terms of the maximum amount of B.O.D. that could be removed with extended foaming. The process was analyzed according to the following development.

If B.O.D. or any similar quantity were considered as a material, a balance was made on the process according to the relation,

$$\text{(input)} - \text{(output)} = \text{accumulation.} \qquad (2)$$

The input to the column was zero since the process was batch. The output was proportional to the rate of foam production and to the concentration of material in the column. Thus,

$$\text{Output} = ka\frac{M}{V} \qquad (3)$$

where M = Material in column

V = Volume of liquid in column

$\frac{M}{V}$ = Material concentration in liquid in column

a = Volumetric rate of foamate (liquid) production

k = Proportionality constant with the units of

$$\frac{\text{Amount of B.O.D. per unit volume of collapsed foam}}{\text{Amount of B.O.D. per unit volume of column liquid}}$$

The proportionality constant, as denoted by its units, could be shown to be the enrichment factor. The accumulation in the column was $-dM$, and the overall balance was

$$ka\frac{M}{V}\,t = -dM \qquad (4)$$

which, when integrated, became

$$k\ln\left(1 - \frac{at}{V_0}\right) = \ln\frac{M}{M_0} \qquad (5)$$

V_0 and M_0 were the initial conditions, and by restrictions in the integration a had to be a constant rate of removal. Since the quantity $(1 - \frac{at}{V})$ could be rearranged to

$$1 - \frac{at}{V_0} = \frac{V_0 - at}{V_0} = \frac{V}{V_0} \tag{6}$$

where V was the liquid left in the column at time t, the derivation became

$$k \ln \frac{V}{V_0} = \ln \frac{M}{M_0} \tag{7}$$

which had no restrictions on how V was removed.

The enrichment factors k were evaluated from the graphical analysis of equation (7). The analysis was in two parts. First, as shown by a typical graph in Figure 3, the volume of liquid in the column and the B.O.D. in the column were plotted as a function of air sparging time. This plot was used to smooth the experimental data, although the actual data points were carried in the final plot as demonstrated by Figure 4. In this final plot and as required by equation (7), the logarithm of the amount of B.O.D. in the column was plotted as a function of the logarithm of the liquid volume in the column. The slope of this line was the enrichment factor. The experimental data and the calculated results necessary for constructing the log-log graphs are presented in Appendix IV-A.

D. Analytical Tests and Procedures

1. Definition of Treatment

The parameters of primary importance to the study were B.O.D.$_5$, solids content (as total, organic, and mineral), and foaming tendency. These tests were routinely performed on the liquid feed to the column, the treated liquid leaving the column, and the collapsed foam and served as the basic measurements for the quantitative evaluation of the foam treatment process. Additional tests included determinations for C.O.D., tall oil content, alkalinity, and pH. These properties could possibly have been significant in describing the liquid feed properties and in correlating the behavior of the foaming process.

Treatment was measured in terms of concentration changes and in terms of the fractional amount of B.O.D. removed from the liquid feed. The concentration changes were expressed as enrichment, $\frac{X_P}{X_F}$, and as bottoms concentration reduction, $\frac{X_B}{X_F}$. The fraction of removal from the feed was

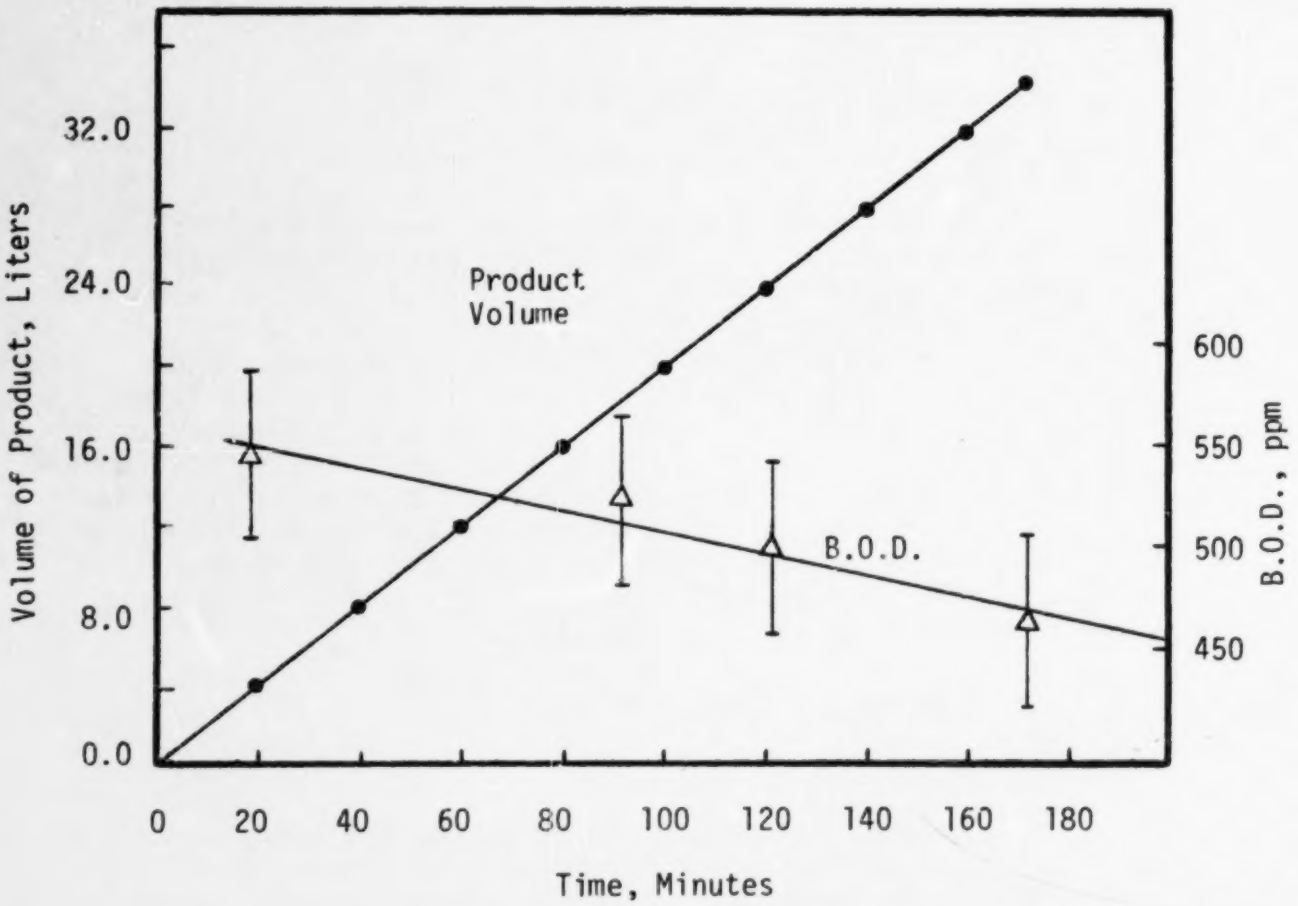

FIGURE 3: TYPICAL GRAPHICAL REPRESENTATION OF EXPERIMENTAL DATA FOR BATCH OPERATION USING RESULTS FOR TEN-FOOT LIQUID COLUMN

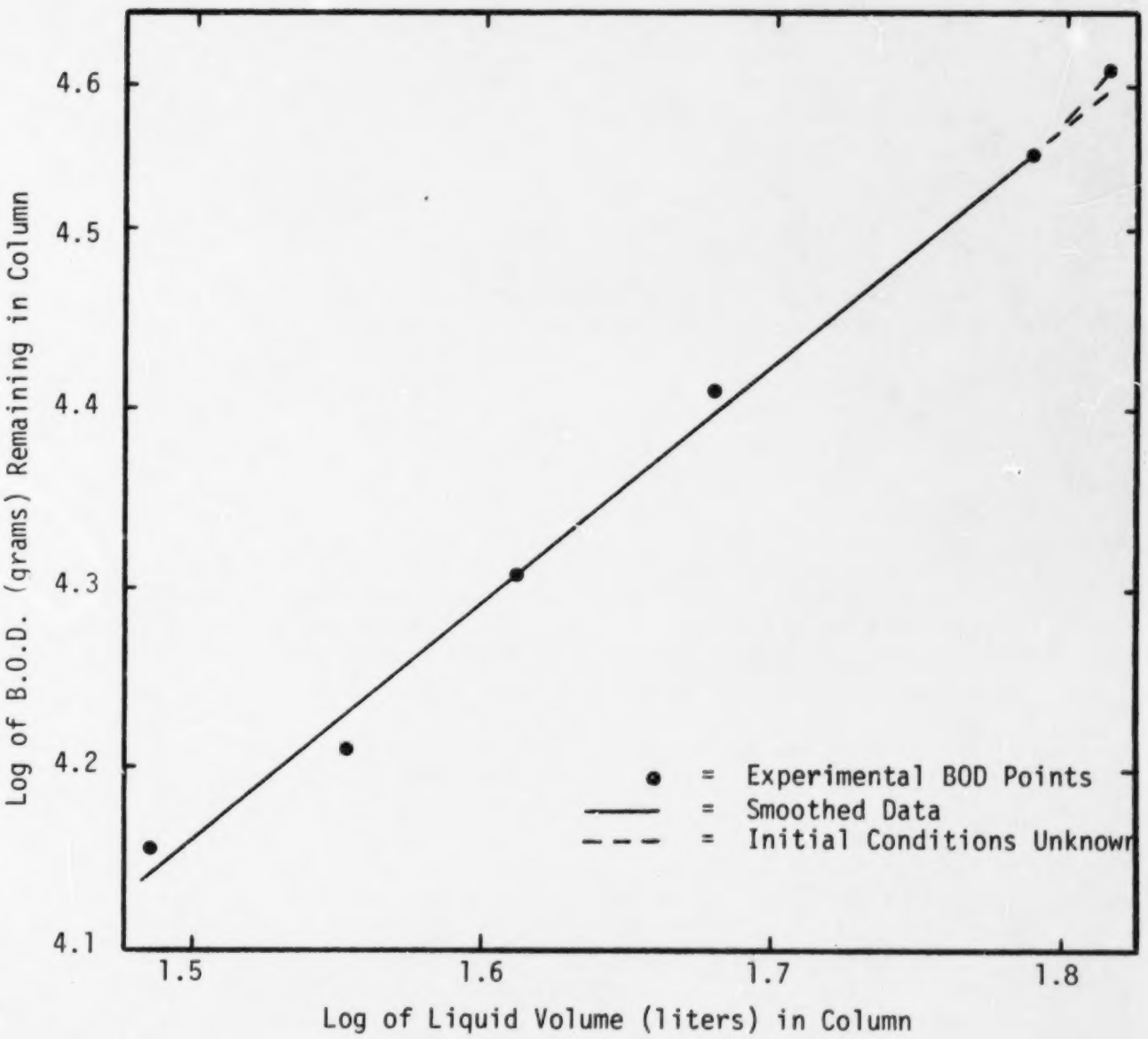

FIGURE 4: GRAPH FOR EVALUATION OF ENRICHMENT FACTOR FOR TEN-FOOT LIQUID COLUMN

$\left[1 - (\frac{X_B}{X_F}) \cdot (\frac{B}{F})\right]$ where $X_B B$ was the B.O.D. in the treated liquid and $X_F F$ was the B.O.D. in the feed. The concentration ratios were indications of the separation potential of the foaming process and showed the partitioning of surface-active constituents between the liquid layer of the gas-liquid interface and the bulk liquid. The fraction of removal, on the other hand, showed the actual performance of the process in terms of how much B.O.D. was removed from the main mill effluent liquid stream. These treatment functions, while described specifically for B.O.D. applied also to C.O.D., solids, and other constituents as needed.

2. B.O.D. and C.O.D.

These determinations followed primary guidelines of national standards. The B.O.D. procedure was that of ASTM D-2329-6ST. The extent of dilution required was established by experiment. The C.O.D. procedure was taken from ASTM D-1252-60, except that reflux times of two hours were used. The long reflux time seemed to produce more uniform results.

3. Solids

Solids determinations were made for the total solids, total organic solids, and mineral content. The total solids was the residue after evaporation of all water at 105°C; total organic solids was taken as the material that could be volatilized at a temperature of 600°C; and the mineral content was the final residue. The procedure was as outlined by standard analytical procedures for waste waters *(24)*. The organic part of the solids included lignin, cellulose, sugars, and fatty and resin acids, among numerous other organic compounds in relatively smaller concentrations. The fatty and resin acids were determined as tall oil by the method of Saltsman and Kuiken *(25)* and were reported as tall oil. All other organic constituents were reported collectively and were evaluated as the total organic content less the tall oil content. An attempt was made to measure the lignin content by the absorption of ultra violet light at 280 millimicrons following the Pearl-Benson *(26)* method. The results from this test, unfortunately, were not reliable due to color interferences from other organic constituents in the mill effluent.

4. Foaming Tendency

Foaming tendency, or foaminess, was a property not directly measurable and had to be expressed in terms of a related

parameter. Numerous physical chemical properties have been employed for this purpose, and some of the more frequently considered have been foam properties--including formation, height, structure, drainage, and composition--and liquid properties of the collapsed foam--including viscosity, surface tension and optical and electrical properties. Bikerman *(27)* defined foaming tendency in terms of the average time a bubble remains entrapped in the foam layer. His function was

$$\sum = \frac{vt}{V} \tag{8}$$

where $\sum$ = average bubble residence time

v = volume of foam generated in time t,

and V = the volume of air introduced.

Carpenter and Gelman *(28)* applied this relationship to kraft mill liquids and devised a test whereby a specified volume of air was sparged at a very low rate into a specified volume of liquid. The height of foam generated was taken as a measure of foaming tendency.

The Carpenter and Gelman approach was tried, but some of the mill effluent samples gave a foaming tendency of zero while very profuse foaming was produced in the experimental apparatus. The cause for these differing results was that some liquids required a certain minimum air sparging rate before a stable foam was generated. The air sparging rate in the test was lower than this critical rate and the sparging rate in the experimental foam column was larger.

The test for foaming tendency was modified in this study so that all liquids gave a useful result. In the modified procedure, the foaming tendency was measured in terms of the maximum height, H^*, that could be generated with a given air rate. Equation (8) was transformed with the substitutions

$v = H^* A_C$,

t = Time

and $V = G \cdot A_C$

where H^* = Maximum foam height

A_C = Column cross sectional area

G = Gas flow rate per unit time per unit cross sectional area

The transformed relationship was

$$\sum = \frac{vt}{V} = \frac{H^* \cdot A_C \cdot t}{G \cdot A_C \cdot t} = \frac{H^*}{G} \quad , \tag{9}$$

and $\sum$, as a measure of foaming tendency, was the ratio of H^* to the specific gas flow rate. For a constant gas flow rate, H^* was proportionately related to $\sum$ and could similarly be taken as a measure of foaming tendency. The test was evaluated experimentally and was found to reflect different H^* values for liquids having visibly different foaming characteristics. The test was imperfect, however, in that H^* was not truly a characterization number; it should have been constant since the equation showed $\frac{H^*}{G}$ to be constant for a selected air rate. H^* was a function of dynamics and was more nearly constant at low air rates. In the experimental column, 6.5 inches in diameter, $\frac{H^*}{G}$ was very nearly constant with less than 6 per cent variation for gas rates up to 0.13 cubic feet of air per minute. At double this gas rate, the ratio declined an additional 6 per cent but was beginning to fall more rapidly. Figure 5 shows these results.

H^* as a measure of foaming tendency was determined in a 6.5-inch diameter liquid column, with an air rate of 0.13 cubic feet per minute, and using a 6-inch liquid depth above the face of the sparger. A smaller 2-inch column was tried, but bubble coalescence caused plug flow of the gas and gave erroneous and unreproducible results.

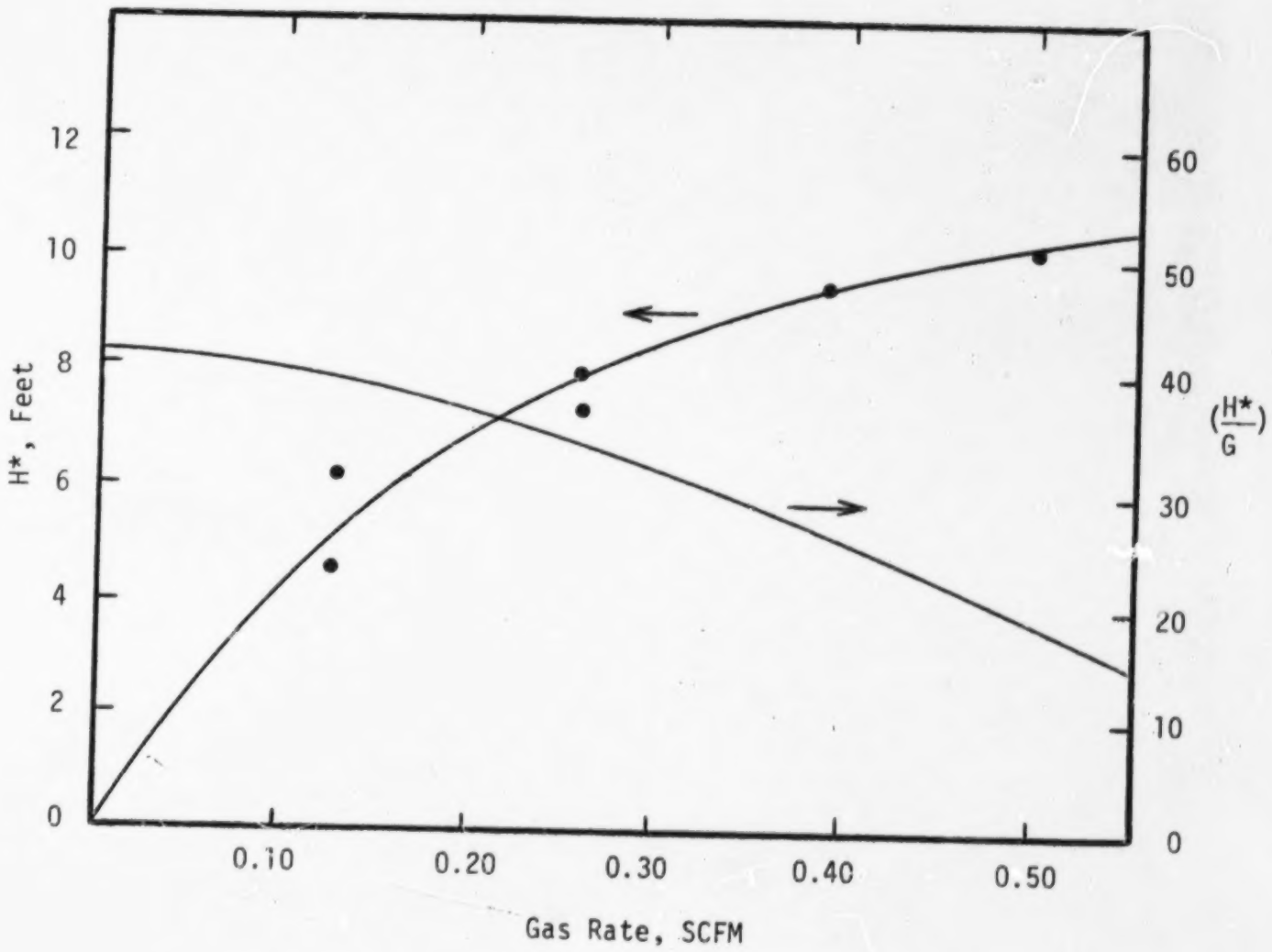

FIGURE 5: FOAMABILITY OF EFFLUENT

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VI. EXPERIMENTAL RESULTS

A. Foaming Tendency

The most significant change produced in the mill effluent by the foam treatment process was the reduction of its tendency to foam. As measured by the method developed for this study, the foaming tendency of the mill effluent was reduced in most experiments at least 40 per cent and, under favorable operating conditions, as much as 60 per cent. The extent to which foaming tendency was reduced was controlled primarily by the gas-to-liquid ratio as shown by the correlation in Figure 6. The most effective operating range of the gas-to-liquid ratio was between 1.0 and 1.5. This operating range achieved most of the foaming tendency reduction, yet it did not require the excessive use of air to gain a small additional increase. In addition to being affected by the gas-to-liquid ratio, the foaming tendency reduction was also affected significantly by the amount of external reflux, a procedure used primarily to control the amount of product produced. Surprisingly, however, a sizeable reduction could be obtained by foaming even when all the product was refluxed. Figure 7 shows the foaming tendency behavior of a typical treated liquid as infinite reflux was approached. In this case the reduction at infinite reflux was 40 per cent with a gas-to-liquid ratio of 1.5.

Other operating variables had less significant effects. In the factorial experiments, raising the liquid pool height from 2 to 8 feet improved the foaming tendency reduction 6 per cent. In other experiments, temperatures ranging from 83°F to 143°F gave no appreciable differences, and the air spargers ranging in average pore size from 25-50 microns to 145-175 microns exhibited approximately the same performance. The maximum foaming tendency reduction under the best conditions was approximately 60 per cent.

B. Foam Generation

The amount of liquid that was transformed into foam depended on the gas-to-liquid ratio and on the amount of foamed product returned to the column as reflux. Figure 8 shows how the volume of the collapsed foam, expressed as a fraction of the feed, increased with increased air-to-liquid ratios when there was no reflux. The significant feature of this result is the intercept, which meant that a minimum amount of air was required to produce any foaming at all. When part of the foamed product was collapsed and returned to the column as reflux, the rate of foamate production increased. Figure 9 shows this effect. Up to a reflux of 4, the rate of foam generation increased 50 per cent; more reflux added only a few percent.

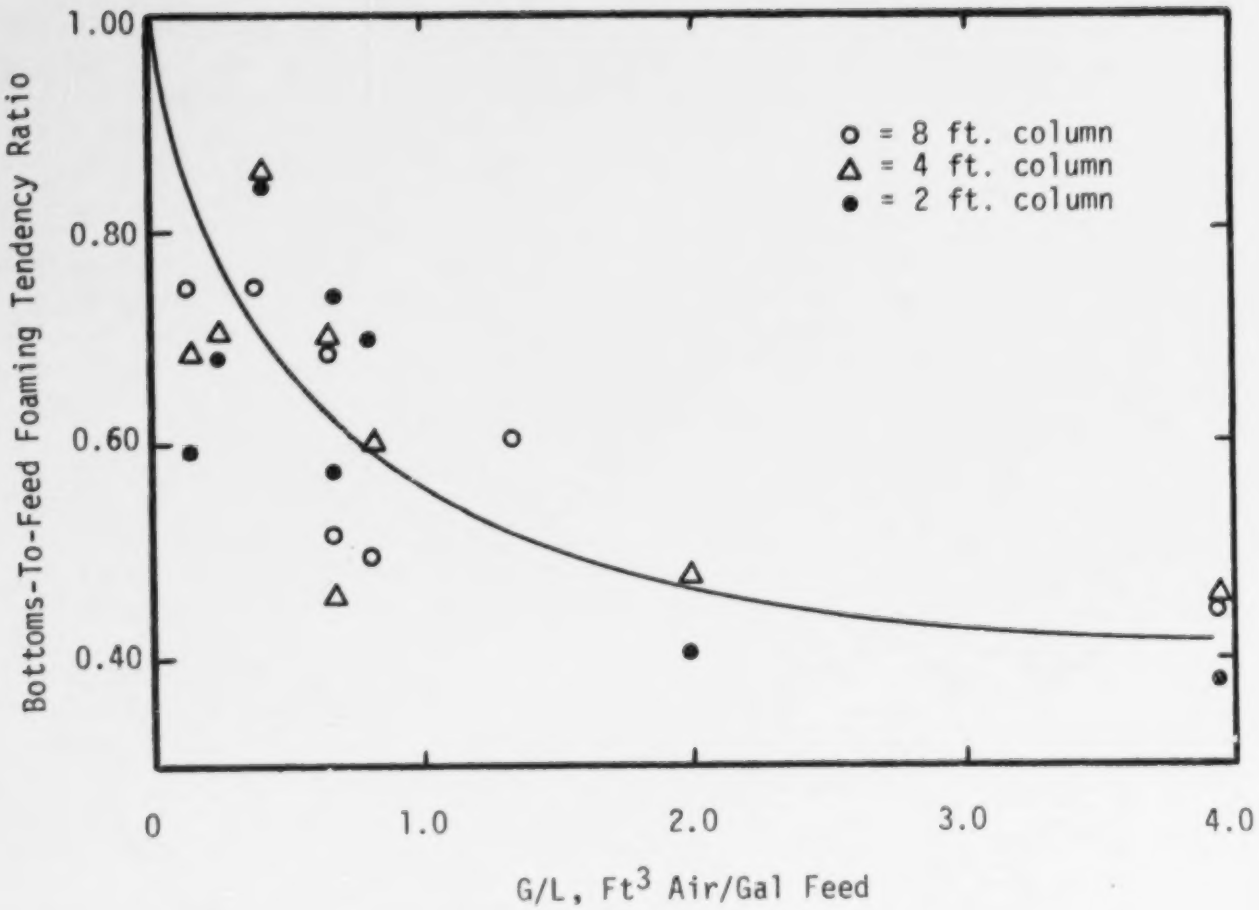

FIGURE 6: REDUCTION IN FOAMING TENDENCY

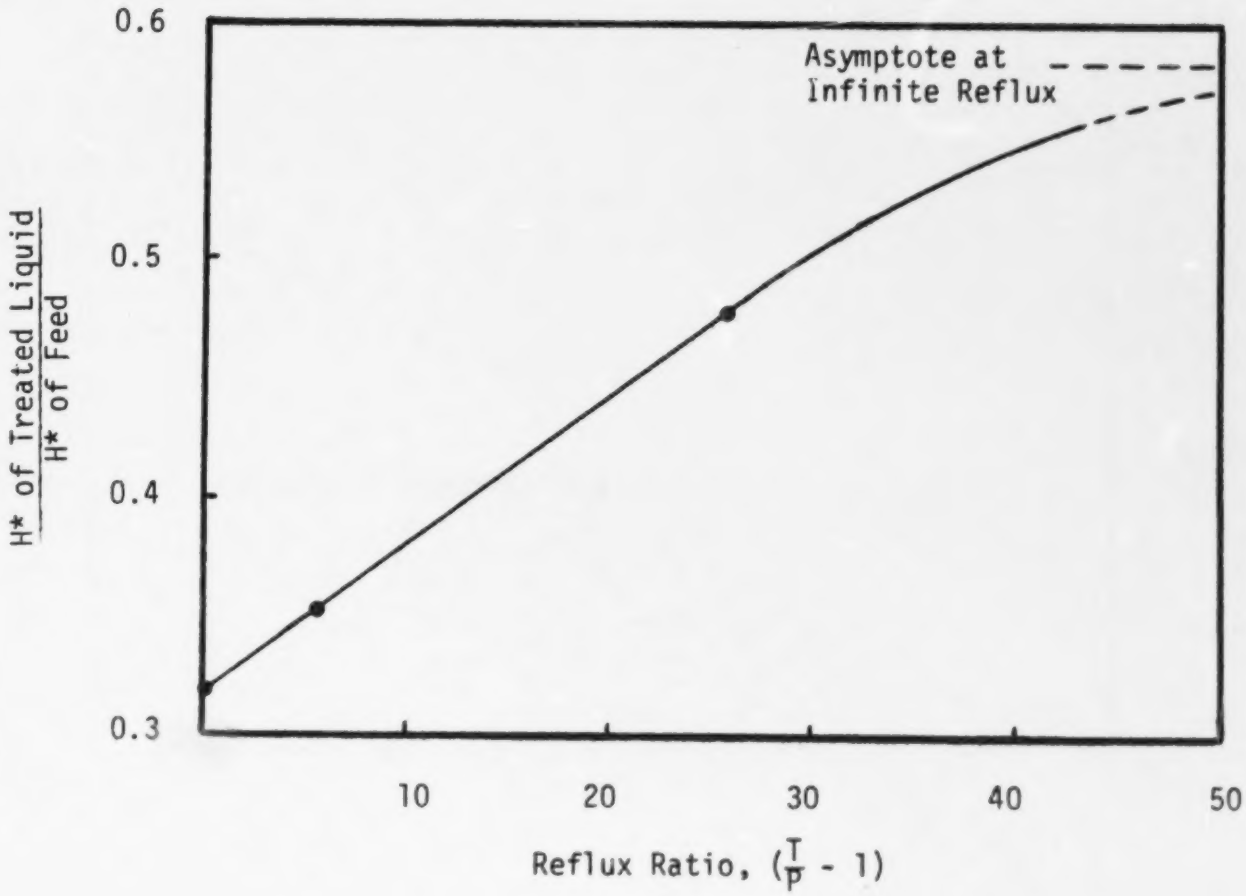

FIGURE 7: FOAMING TENDENCY OF TREATED LIQUID AS AFFECTED BY REFLUX

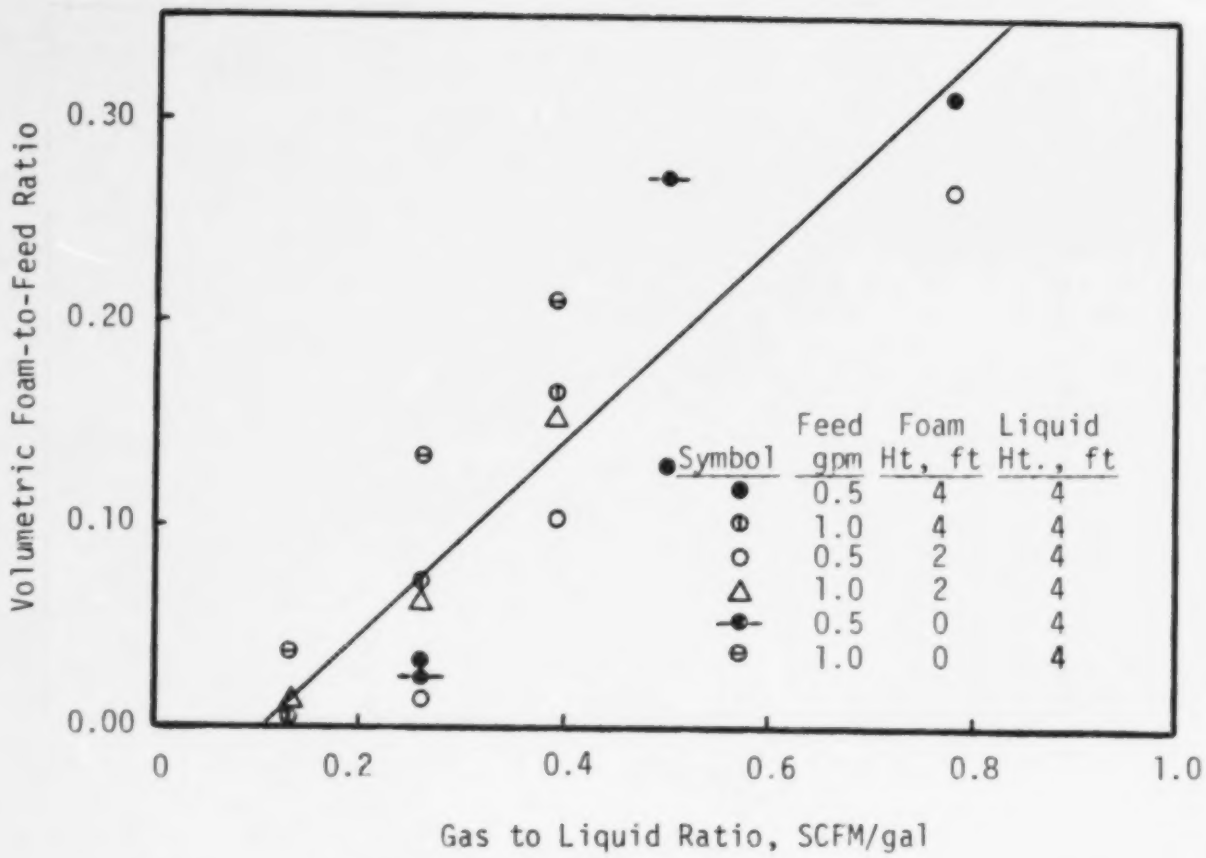

FIGURE 8: RATE OF FOAM PRODUCTION AS AFFECTED BY GAS-TO-LIQUID RATIO

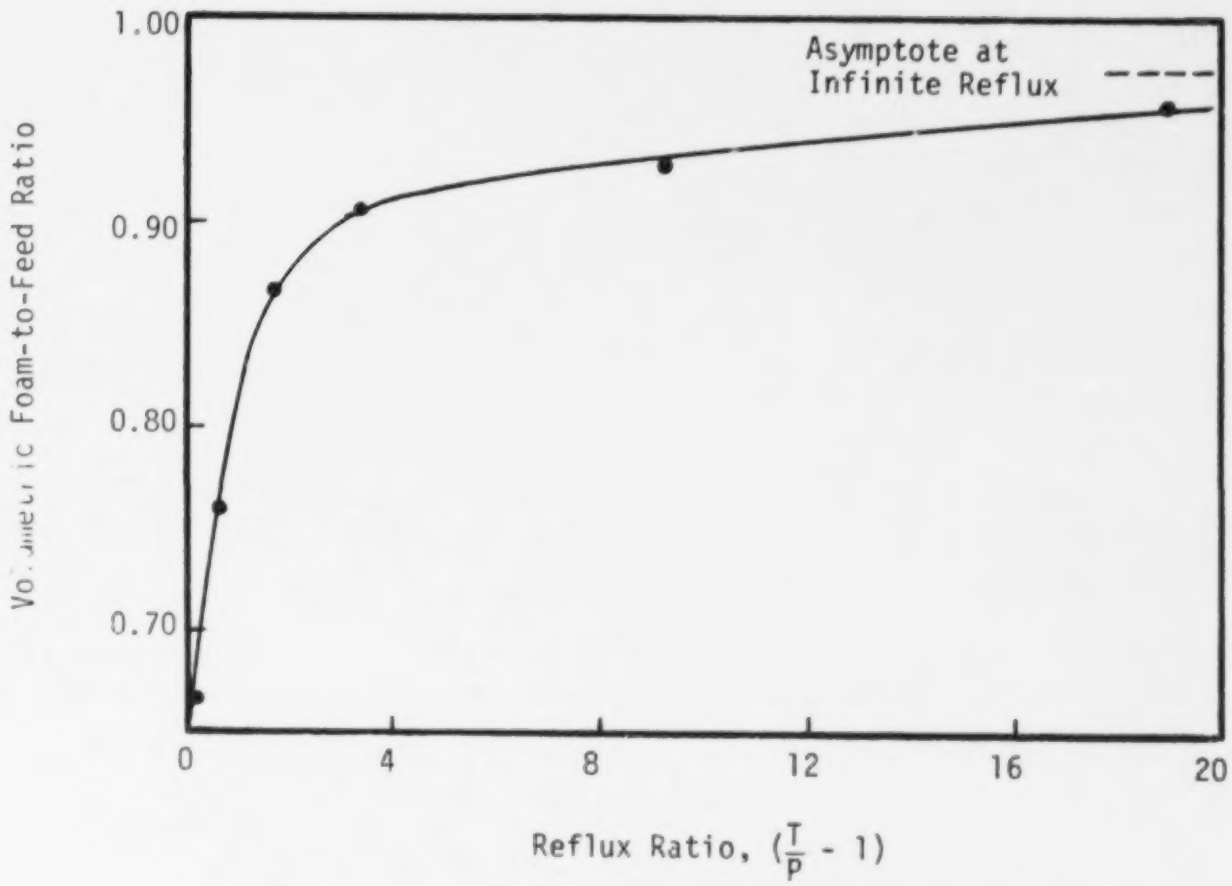

FIGURE 9: RATE OF FOAM PRODUCTION AS AFFECTED BY REFLUX RATIO

C. B.O.D., C.O.D., and Solids Removal

The reduction of B.O.D. by foam separation was the primary objective of this study. Unfortunately, however, the process did not show the desired capability under the conditions tested. Throughout the course of the experimental work, foam separation was found to produce only limited amounts of B.O.D. removal. In the steady flow experiments, approximately 10 per cent of the B.O.D. could be removed from the liquid stream. The results were practically invariant with respect to changes in liquid flow, gas flow, column height, air sparger porosity, feed position, amount of reflux, and temperature. No combination of these physical operating variables produced any significant improvement in treatment.

Not all of the 10 per cent B.O.D. reduction was due to concentration changes; some of the reduction was from the partitioning of liquid between the treated liquid stream and the foamed product. The total treatment was expressed by

$$\left[1 - \left(\frac{X_B}{X_F}\right) \cdot \left(\frac{B}{F}\right)\right] \cdot 100$$

where $\left(\frac{X_B}{X_F} \cdot \frac{B}{F}\right)$ was the fraction of B.O.D. left in the treated liquid,

$1 - \left(\frac{X_B}{X_F}\right)\left(\frac{B}{F}\right)$ was the fraction of B.O.D. in the product stream,

$\frac{X_B}{X_F}$ was treated liquid-to-feed concentration ratio,

and $\frac{B}{F}$ was treated liquid-to-feed flow ratio.

The foaming column was operated with reflux so that the product was removed to yield 5 per cent of the feed liquid as product and 95 per cent as treated liquid or bottoms. Thus, $\frac{B}{F}$ was 0.95. The concentration ratio, $\frac{X_B}{X_F}$, was found also to be approximately 0.95. The treatment then was

$$\left[1 - (0.95)\ (0.95)\right]\ 100 \approx 10\%$$

The B.O.D. in the mill effluent was to some degree related to the C.O.D. and the total solids content. Measurements of the C.O.D. showed a reduction of approximately 15 per cent, which was slightly greater than the B.O.D. reduction. There were no appreciable changes produced by varying the operating variables including gas flow, liquid flow, liquid column height, foam

height, and temperature. The solids content was not measurably reduced under any conditions.

Figures 10 and 11 show the B.O.D. and C.O.D. treatment analyzed in terms of the gas-to-liquid ratio, and Figures 12 and 13 present the study of temperature effects for three column heights. The experimental points had considerable scatter (standard error in B.O.D. ± 12 per cent); however, considering the number of measurements taken, it is evident that a practical degree of treatment was not obtained unless, of course, the foam separation could be applied repetitively as the stages in distillation. The data as shown included the partitioning factor, $\frac{B}{F}$, and without it the B.O.D. and C.O.D. reductions would not even be as large as indicated. The unreduced experimental results are tabulated in Appendices I-A and I-B.

The factorial experiments were designed to reveal the effects of column height, gas rate, and liquid rate and were the source of the data for Figures 10 and 11. When these data were analyzed again for the first order effects of column height, gas rate, and liquid rate, the results shown in Table 1 were obtained. Again the calculations were made with the function $\left[1 - \left(\frac{B}{F}\right)\left(\frac{X_B}{X_F}\right)\right]$, where X was the B.O.D., C.O.D., and solids corresponding to each of the three columns of data. No statistically significant variations were found. The B.O.D. reduction (0.25) for the 8-foot column was believed to be in error. Supplementary experiments confirmed that less reduction than 0.25 should have been indicated.

The effects of feed and reflux position were investigated with a column having a liquid pool height of 4 feet and a foam height of 8 feet. Positions were tried with the feed and reflux (1) both at the liquid pool surface, (2) both at the middle of the foam column, (3) the reflux at the top of the foam and the feed at the middle of the foam column, and (4) the reflux at the top of the foam and the feed at the pool surface. The treatment (Appendix III) was no different from that already found in all other experiments.

Theoretical consideration indicated that refluxing of part of the collapsed foam product could have an effect on the enrichment of B.O.D. in the foam and on the stripping of B.O.D. from the treated liquid. The reasoning was based on the fact that some reflux would enrich the concentration of B.O.D.-containing compounds in the column and the enrichment would increase the rate of the separation process as would be experienced in similar operations, e.g., distillation. If the reflux were infinite, on the other hand, there would be no reduction in

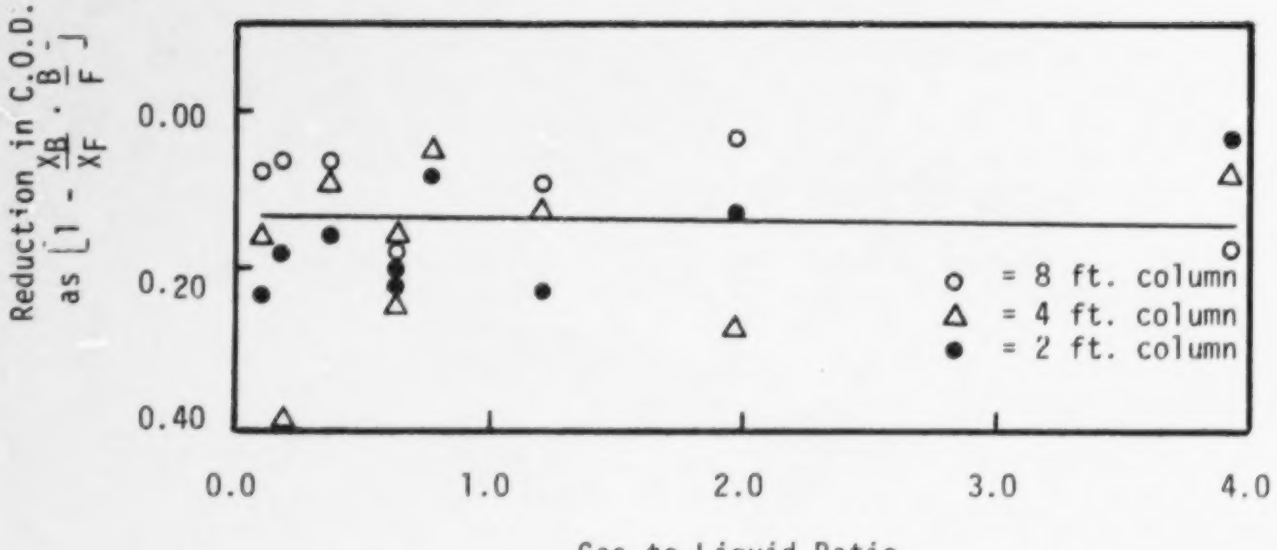

FIGURE 10: CHEMICAL TREATMENT AS FUNCTION OF GAS-TO-LIQUID RATIO

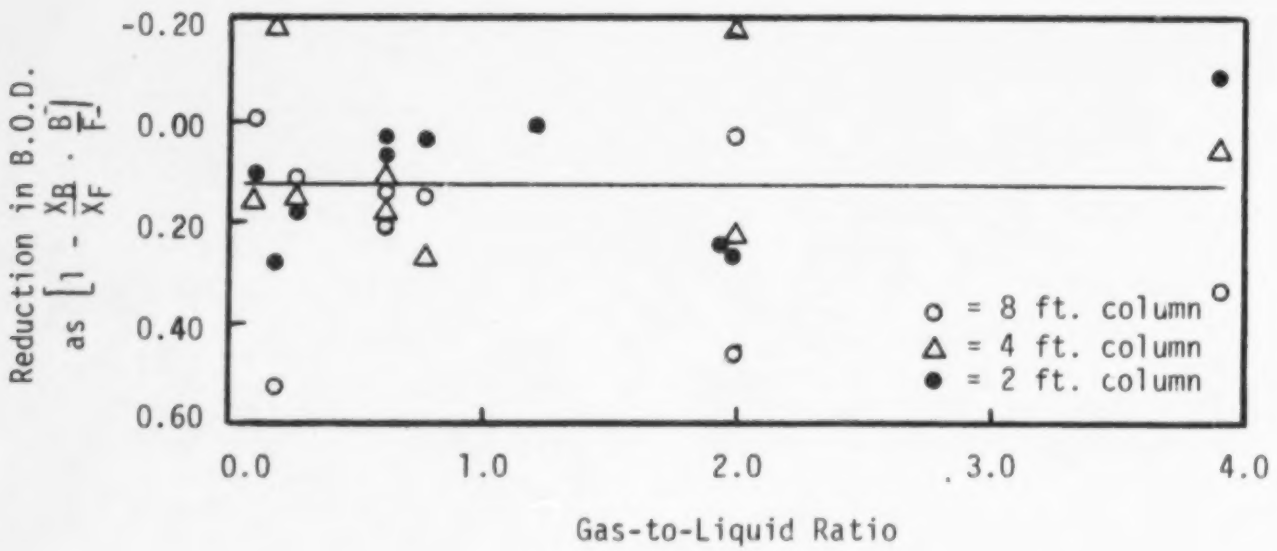

FIGURE 11: BIOLOGICAL TREATMENT AS FUNCTION OF GAS-TO-LIQUID RATIO

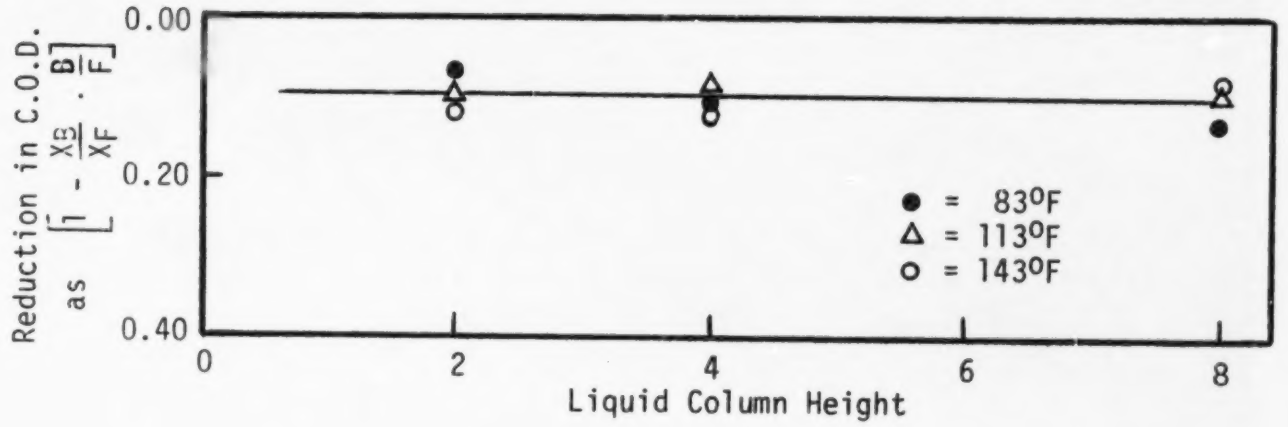

FIGURE 12: C.O.D. REDUCTION AS FUNCTION OF TEMPERATURE AND LIQUID COLUMN HEIGHT

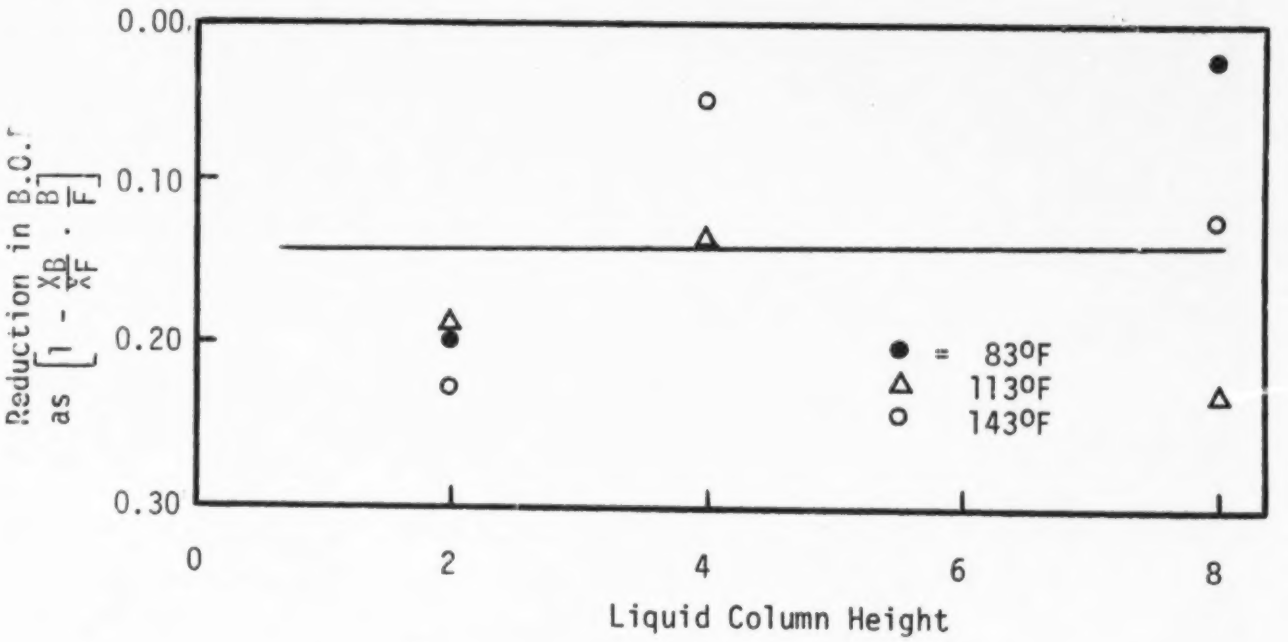

FIGURE 13: B.O.D. REDUCTION AS FUNCTION OF TEMPERATURE AND LIQUID COLUMN HEIGHT

TABLE 1

SUMMARY OF RESULTS FOR FACTORIAL FOAM SEPARATION EXPERIMENTS

Operating Variables and Their Magnitudes	Treatment in Terms of Fraction Reduced For			
	Foaming Tendency	B.O.D.	C.O.D.	Solids
Liquid Feed (GPM)				
0.2	0.49	0.13	0.15	0.03
0.6	0.33	0.15	0.19	0.08
1.0	0.30	0.14	0.12	-0.05
Column Height (ft.)				
2	0.36	0.10	0.16	0.01
4	0.37	0.08	0.18	0
8	0.42	0.25	0.12	-0.07
Air Rate (CFM)				
0.13	0.33	0.13	0.19	-0.05
0.39	0.38	0.13	0.16	0.08
0.78	0.43	0.17	0.12	0.03

B.O.D. because a steady state mass balance would require all the B.O.D. compounds to remain with the treated liquid. Concentration changes would exist in the column, however. Measurement of the B.O.D. concentration in the refluxing liquid did show some increase at infinite reflux, as would be expected. Somewhere between the no reflux and infinite reflux conditions, there should have been an optimum amount of reflux. Experimental data were collected over a wide range of refluxing conditions. Some of the data indicated a favorable change, but repeated measurements failed to establish a consistent increase in treatment at any reflux. It was concluded that reflux did not have an appreciable effect. The treatment as a function of reflux is given in Figure 14, and the experimental data are tabulated in Appendix III.

Supplementary experiments investigated the treatment that could be obtained with very short liquid columns. It was found (Appendix III) that liquid columns down to one-half foot were practically as effective as all others studied.

D. Batch Experiments

Batch experiments were designed to determine the maximum amount of treatment that could be obtained in a single foam separation stage and to examine more closely the B.O.D. enrichment factor, which was the B.O.D. concentration in the foam divided by the B.O.D. in the liquid pool. The effect of initial liquid pool height, foam height, air sparger porosity, air rate, temperature, and acidification (pH adjustment) were investigated. The treatability of several different mill streams was also studied. The experimental results are given in Appendix IV-A.

The enrichment factors evaluated from batch experiments are presented in Appendix IV-B. All the factors were in the range of 1.0 to 1.5 and indicated a very weak dependence on the operating variables observed. Enrichment ratios in this range correspond to the 5-10 per cent levels of treatment found in the steady flow experiments. The exact effect of changing the operating conditions was not discernable. For instance, the enrichment factor as a function of temperature was 1.22, 1.34, and 1.44 for 80°, 110°, and 136°F, respectively, and showed a trend toward higher enrichment with increased temperature. This trend, however, was so slight that a recalculation of the results on the performance of additional experiments could have nullified or even reversed it.

As noted in the calculated data, some experiments exhibited a discontinuity between the feed liquor B.O.D. point and the

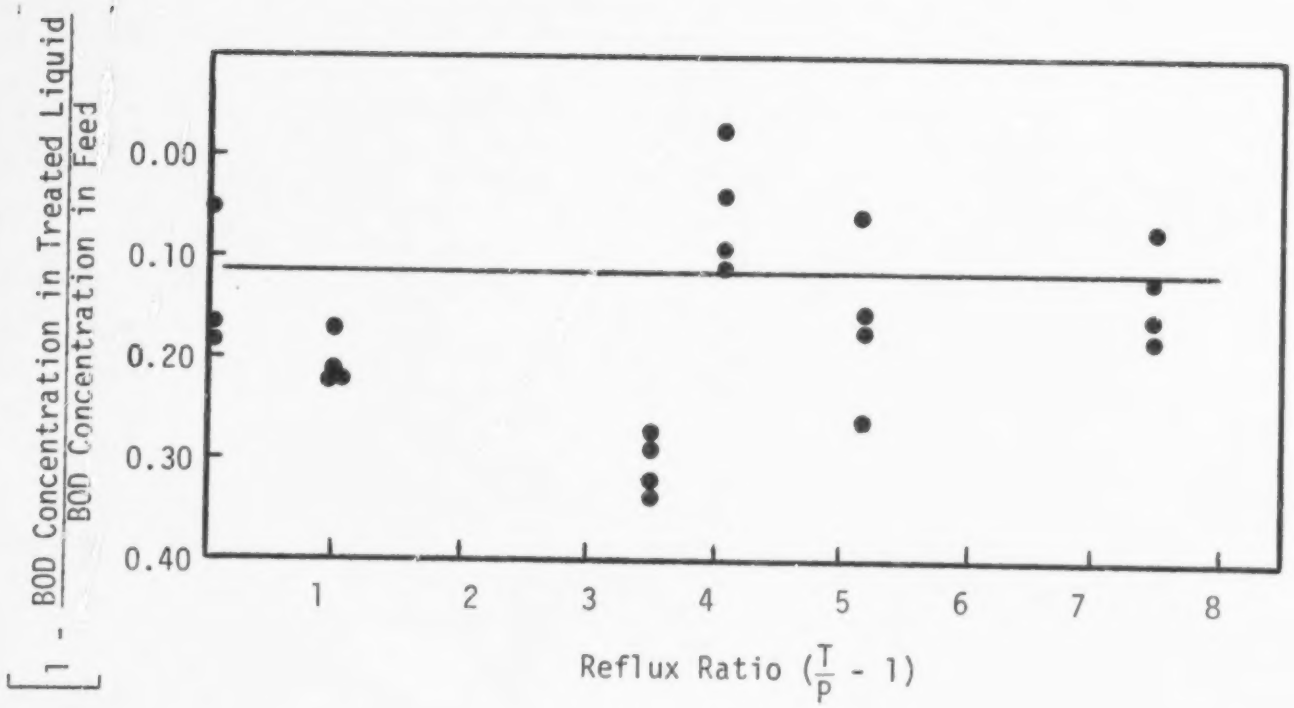

FIGURE 14: REDUCTION IN B.O.D. CONCENTRATION AS A FUNCTION OF REFLUX

intercept of the straight line which seemed to fit the B.O.D. measurement as a function of sparging time. In several experiments when this discontinuity was present, the enrichment factor was usually small and near 1.00 to 1.05. In others when the discontinuity was not apparent, larger enrichment factors were calculated tending to be closer to 1.5. It was thought that enrichment between 1.0 and 1.5 was definitely occurring, but differences within this range could not be regarded as significant.

The acidification experiments were different from others in the study in that a precipitate formed with decreasing pH. The data in Appendix IV-A, Table 7 shows the B.O.D. to be lowered also with decreasing pH. This B.O.D. removal was probably due to precipitate formation which carried with it B.O.D.-producing materials. An attempt was made in the experiment to keep the precipitate in suspension by stirring as the pH was reduced. At each pH studied the reduced B.O.D. (at time = 0) was brought about by the air initially sweeping out a considerable amount of the precipitate.

With regard to the maximum B.O.D. reduction, the batch experiments proved conclusively that foam separation was limited. In the total of some 20 to 30 valid batch experiments, the B.O.D. was never reduced more than 15 per cent even after one to two hours of sparging, and the liquid volume was reduced over 60 per cent. On the average, B.O.D. was reduced 5 to 10 per cent.

E. Chemical Analyses

The basic measurements of B.O.D., C.O.D., and solids content revealed practically no change in the treated liquid as compared with the feed material and indicated there was probably very little change in chemical composition. The fact that foaming tendency was reduced by foam treatment would indicate that a chemical change had taken place; however, the extent could be small since foaming could be greatly affected by only trace quantities of dissolved materials. It was suspected that the fatty acid and resin acid content of southern pine was one of the chief materials responsible for the intense foaming in southern kraft pulp mills, and tests were devised to measure changes in these materials (tall oil) specifically. Analyses were made of the feed, treated liquid, and foamed product streams in the flow experiments, of the liquid and foam in the batch experiments and of some foams and liquids associated with the waste treatment system at Georgia Kraft Company's Krannert Division mill. The results are given in Appendix V. The analyses are reported as total solids, ash or mineral content, tall oil, and organic materials exclusive of tall oil.

The analyses for the flow experiments (Appendix V, Table 1) confirmed that no major change in total solids or organic content took place, and they showed that the tall oil content, amounting to about 5 to 6 per cent of the total organic materials, was slightly, but measurably, reduced. Since the tall oil concentration measurements were accurate to only one significant figure, the small changes in tall oil contents were not detected in some cases. The average of all results, having both feed and treated liquid analysis, showed a tall oil content reduction of about 30 per cent. In batch experiments a definite tall oil removal was found, and the foam phase at the beginning of the experiment was notably enriched. Further, the liquid remaining in the column at the end of the batch experiments was definitely reduced in tall oil by at least 50 per cent and probably much better. The batch experimental approach was believed to give more reliable data in studying the foaming process.

It is notable that foams taken from the primary and secondary clarifiers of Georgia Kraft Company's Krannert Division were more dense and contained greater solids content than those generated in the laboratory. This condition probably resulted from very stable and well-drained foams which did not allow the residual solids to return to the bulk liquid beneath. Foam from the primary clarifier effluent contained 0.64 per cent solids, of which 28.8 per cent was tall oil. The liquid from which this foam came had 0.15 per cent solids and a tall oil content of only 0.006 per cent. Analytical results for the secondary clarifier foam had the same trend except the solids concentrations were larger.

VII. DISCUSSION OF RESULTS

A. Applications of Foam Separation

The ideal objective of a foam separation process for treating kraft mill waste would be economical simultaneous reduction of B.O.D. and foaming tendency. In such a process it would be necessary to concentrate highly the B.O.D. and foam producing constituents in the foamate which should represent a small fraction of the raw effluent volume; the concentrated foamate stream should then be treated more economically than the total volume of raw waste. If B.O.D. reductions comparable to other treatment methods could be obtained, the added benefit of foam prevention would make the process very attractive.

Unfortunately, the results obtained here indicate that significant B.O.D. removal does not occur upon foaming. And while the process may find justification in some specific cases, it is not likely that the process would generally be economical based on foaming tendency reduction alone.

While the tendency to foam was not completely removed, the reduction was consistent, uniform, and probably more effective than additives usually employed to control foaming. In the operation of pulp mills, additives have been found unpredictable in controlling foaming and have been exceedingly difficult to apply in trace amounts as evidenced by the persistence of foam even with liberal applications of numerous additives, all of which presumably yield satisfactory laboratory tests.

If it were found desirable to use the process to reduce foaming tendency, the data in this report could be used for preliminary design. Experiments showed that under practically any set of conditions a reduction of at least 40 per cent could be obtained, and as much as 60 per cent was possible under the most favorable conditions. Since the foaming tendency of mill effluent was found to vary from a low to a high value by approximately this amount during normal operation, such a foam treatment system could be employed to control the foaming tendency of the mill effluent below what is now the minimum foaming tendency. The ultimate effect would be to aid the prevention of foam flocs or "snow" which at times are formed in the effluent treatment systems of kraft mills.

The process could be operated with a gas-to-liquid ratio of 1.0 to 1.5 SCFM/gal and with as little as 2 feet of liquid depth. Since the process was found effective in reducing foaming tendency even as infinite reflux was approached, the reflux would be adjusted to give perhaps as little a foam

product rate as 0.1 per cent of the feed rate. The separated product (collapsed liquid) would be disposed of by any of numerous methods such as burning in the chemical recovery boilers. For a mill with 15 million gallons of effluent per day, the product would be approximately 10 gallons per minute which could be easily handled.

It is conceivable that the addition of other chemicals to the raw effluent could improve the treatment obtained by foaming. Although study of additives was beyond the scope of this study, one series of experiments was run in which the pH was adjusted over a wide range. Acidification produced a precipitate which was removed by the foam, and this resulted in a significant B.O.D. reduction. The cost of acidification and final neutralization of a large volume of kraft mill effluent would be prohibitive, however. Also, it is likely that the precipitated material could be removed more easily by filtration or settling than by foaming. It is possible, however, that other additives could be found which would tend to cause the dissolved organics to become more surface active or to attach themselves to those surface-active materials present.

It is also possible that by using more than one foam column in series improved treatment could be obtained. The approach, however, does not now appear feasible for two reasons. One is the apparent linkage between foam treatment and tall oil content. Since the tall oil content of kraft mill effluent is low (less than 5 per cent of organics), treatment could be limited regardless of the process used. This is supported by the fact that, when the liquid was given extended treatment in the batch experiments, the B.O.D. could be reduced a maximum of only about 10 per cent. In the batch experiments, the liquid was foamed until no more foam could be expelled from the column and the liquid volume was decreased to about 40 per cent of its original volume.

The second reason is the treatment found experimentally is so low that an impractical number of stages would be required to achieve a commercially effective separation. All calculations relating to the flow experiments indicated that the liquid treatment ranged from practically no reduction in B.O.D. to a maximum reduction of 5 per cent with a most probable value about the middle of the range. Calculations were made for a number of multiple column arrangements using this degree of treatment in each column, and the number of columns required to obtain practical separations was always prohibitive.

B. Relationship of Tall Oil Content to Foam Treatment

Analysis for tall oil showed that this material, amounting to approximately 5 per cent of the total organic material, was

measurably reduced by foam treatment. The reduction in the steady flow experiments was probably as much as 50 per cent, but the accuracy in measuring such small amounts (0.004 per cent by weight) made the result only approximate. In the batch experiments, the tall oil content decreased from 0.004-0.006 per cent to about 0.001 per cent after extended foaming and the tendency to foam was depleted even with increasing air flow. These findings indicated that foam treatment was related at least partially to the tall oil content of the mill effluent.

The relationship between tall oil content and the reduction of B.O.D. and C.O.D. could be estimated from the oxidation reactions of typical fatty acids and resin acids chemically approximating the major tall oil constituents. With stearic and abietic acid representing the typical components, it could be calculated that the maximum B.O.D. attributable to the tall oil components would be only about 10-12 per cent of the total B.O.D. of the raw feed. Thus, a 50 per cent removal of the tall oil would correspond to the 5-6 per cent B.O.D. reductions which were found experimentally.

Foaming tendency was also found to be related at least partially to the tall oil content of the mill effluent. The batch experiments demonstrated the relationship; these studies operated as long as foaming could be sustained even with increasing air ratios and the tall oil content diminished with time. In the studies of reflux ratios in the flow experiments, where it was found that foaming tendency was reduced even at infinite reflux, it is suspected that tall oil was being concentrated in the foam and separating. Thus, there is a possibility that some of this by-product might be reclaimed in the process. However, the tall oil normally found in the effluent amounted to only about 4 to 5 tons per day or no more than 5 per cent of the tall oil available to the mill, and recovery of half of this amount would not provide enough economic incentive for installing the process.

C. Economics of the Process

The removal of the B.O.D. was too small to warrant any practical considerations. The process, however, was moderately effective in reducing foaming tendency and might conceivably be used for this purpose.

The experimental column was approximately 0.2 square feet in cross section and was operated successfully with liquid rates up to 1.0 GPM. The required air rate to get optimum foaming tendency reduction was from 1.0 to 1.5 SCFM of air per gallon of liquid. These data reduce to 5 GPM/ft^2 and 5.0 to 7.5

SCFM/ft^2 and may be used for preliminary sizing of a commercial process for reducing foaming tendency.

A rough cost estimate was made for the Krannert Division of the Georgia Kraft Company to relate the cost of foam treatment to the cost of chemical additives to control foaming in the effluent treatment plant. For a 15 million gallon per day liquid rate and a 7.5 SCFM/gal air rate, the estimate (Table 2) gave a unit cost of 4.97 cents/1000 gallons exclusive of the cost for treating any foamed product that might be removed. Chemical additives presently control foam at a cost considerably less than this. The reduction of foaming tendency by physical treatment, therefore, has an unfavorable cost, although further refinements of the process might reduce this cost to approximate that required by chemical additives.

Rose and Sebald *(5)* recently estimated the cost of a foam separation process for treating domestic sewage at the rate of 10 million gallons per day with a liquid loading of 5 GPM/ft^2 and an air flow of 3 SCFM/ft^2. The unit cost was approximately two cents per 1000 gallons. Scaling this result according to their recommendations to a 15-million-gallon-per-day plant with an air flow of 7.5 SCFM/ft^2 gives 4.5 cents per 1000 gallons. This cost is slightly lower than that estimated in this study for treating kraft mill effluent. The major factor causing Rose and Sebald's modified estimate to be lower is a much smaller power requirement. Capital costs, on the other hand, were estimated to be about 0.85 cents per 1000 gallons greater for the domestic sewage system than for the kraft mill effluent system. With all factors considered, both estimates indicate a cost of around 5 cents per 1000 gallons, which is too high to be of immediate interest.

D. Research for Improving Foam Treatment

Foam treatment as practiced in this study was definitely limited. The process, nevertheless, may still have potential if chemical additives can be found to increase the surface activity of non-foamable compounds in the liquor or to attach these compounds to others which are surface active. Research in this area was beyond the scope of this project. It is felt that a fundamental study should be undertaken to find means for accomplishing separation; subsequent investigations would then attempt practical applications.

TABLE 2

ECONOMIC ANALYSIS OF FOAM SEPARATION*

			Total Costs
I.	Capital Costs		
	A. Equipment Costs		
	Tanks and Footings	$ 41,500	
	Pumps	28,000	
	Air Compressors	120,000	
	Foam Breakers	28,200	
	Total Equipment		$217,700
	B. Equipment Installation (150% of equipment costs)		326,500
	C. Total Capital		544,200
II.	Annual Operating Costs		
	A. Capital with 20-Year Life		
	Depreciation - 5%		
	Interest - 7%		
	Taxes & Ins. - 6%		
	18%	$ 97,900	
	B. Power at $100 per HP year	145,500	
	C. Maintenance at 2% of Capital Cost	10,900	
	D. Labor	7,000	
	E. Total Operating Costs		$261,300
III.	Unit Operating Cost: 4.97 cents/1000 gallons		

*Basis: Liquid rate = 15 million gallons/day; air rate = 7.5 standard cubic feet/minute/gallon liquid.

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APPENDIX I-A
FACTORIAL EXPERIMENT DESIGN

TABLE 1
CONFOUNDING OF FACTORIAL EXPERIMENTS INTO THREE BLOCKS(1)

Block I	Block II	Block III
L_0, G_0, C_0	L_0, G_0, C_2	L_0, G_1, C_0
L_1, G_1, C_0	L_1, G_1, C_2	L_1, G_2, C_0
L_2, G_2, C_0	L_2, G_2, C_2	L_2, G_0, C_0
L_0, G_2, C_1	L_0, G_1, C_1	L_0, G_0, C_1
L_1, G_0, C_1	L_1, G_2, C_1	L_1, G_1, C_1
L_2, G_1, C_1	L_2, G_0, C_1	L_2, G_2, C_1
L_0, G_1, C_2	L_0, G_2, C_0	L_0, G_2, C_2
L_1, G_2, C_2	L_1, G_0, C_0	L_1, G_0, C_2
L_2, G_0, C_2	L_2, G_1, C_0	L_2, G_1, C_2

---

(1) Each block run with one feed. Each experiment defined by a liquid rate, L; a gas rate, G; and a liquid column height, C. The values for each were:

L_0 = 0.2 GPM	G_0 = 0.13 SCFM	C_0 = 2 ft.
L_1 = 0.6 GPM	G_1 = 0.39 SCFM	C_1 = 4 ft.
L_2 = 1.0 GPM	G_2 = 0.78 SCFM	C_2 = 8 ft.

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APPENDIX I-B
EXPERIMENTAL DATA FOR FACTORIAL EXPERIMENTS

TABLE 1
EXPERIMENTAL DATA FOR BLOCK I OF FACTORIAL EXPERIMENTS

Experimental Conditions	Feed					Collapsed Foam (Tops)					Treated Liquor (Bottoms)				
	BOD ppm	COD mg/l	Solids %	N_a ppm	pH	BOD ppm	COD mg/l	Solids %	N_a ppm	pH	BOD ppm	COD mg/l	Solids %	N_a ppm	pH
L_0, G_0, C_0	360	1005	0.114	250	8.0	440	1310	0.139	260	8.0	380	960	0.120	225	7.9
L_1, G_1, C_0	360	1060	0.112	220	8.1	440	1140	0.125	260	8.2	300	880	0.117	250	8.1
L_2, G_2, C_0	300	1070	0.127	225	8.2	320	1180	0.125	240	8.2	200	910	0.124	245	8.1
L_0, G_2, C_1	300	895	0.118	250	7.9	300	1230	0.131	255	8.3	220	865	0.112	260	8.3
L_1, G_0, C_1	240	850	0.172	240	8.2	400	880	0.134	250	8.1	340	785	0.123	230	7.9
L_2, G_1, C_1	220	1060	0.137	235	8.2	300	1140	0.130	250	8.2	280	815	0.117	245	8.2
L_0, G_1, C_2	220	880	0.117	230	7.1	240	1005	0.132	255	7.8	180	770	0.092	250	8.0
L_1, G_2, C_2	240	770	0.121	250	8.1	280	800	0.121	255	8.2	260	705	0.116	250	8.2
L_2, G_0, C_2	260	790	0.120	245	8.0	300	1090	0.146	255	8.0	240	690	0.118	250	8.2

APPENDIX I-B
(Continued)

TABLE 2
EXPERIMENTAL DATA FOR BLOCK II OF FACTORIAL EXPERIMENTS

Experimental Conditions	Feed					Collapsed Foam (Tops)					Treated Liquor (Bottoms)				
	BOD ppm	COD mg/l	Solids %	Na ppm	pH	BOD ppm	COD mg/l	Solids %	Na ppm	pH	BOD ppm	COD mg/l	Solids %	Na ppm	pH
L_0, G_0, C_2	260	375	0.112	215	9.1	400	1240	0.137	205	8.8	240	305	0.107	195	9.1
L_1, G_1, C_2	220	660	0.103	200	9.2	220	1002	0.114	190	9.1	220	530	0.102	200	9.1
L_2, G_2, C_2	160	335	0.102	185	9.2	200	335	0.109	185	8.9	180	335	0.109	185	8.8
L_0, G_1, C_1	320	640	0.097	185	8.2	340	850	0.106	170	8.5	280	610	0.099	175	8.7
L_1, G_2, C_1	280	640	0.099	185	8.8	260	735	0.101	195	8.7	240	590	0.114	175	8.6
L_2, G_0, C_1	280	735	0.094	185	9.0	500	1002	0.144	190	8.8	220	590	0.097	180	9.0
L_0, G_2, C_0	180	370	0.102	195	8.2	240	640	0.106	210	8.0	160	355	0.104	175	8.1
L_1, G_0, C_0	240	480	0.101	185	8.1	320	1002	0.122	200	8.0	120	465	0.105	175	8.1
L_2, G_1, C_0	160	415	0.103	170	8.1	180	480	0.113	200	8.0	120	415	0.100	155	8.0

APPENDIX I-B
(Continued)

TABLE 3
EXPERIMENTAL DATA FOR BLOCK III OF FACTORIAL EXPERIMENTS

Experimental Conditions	Feed					Collapsed Foam (Tops)					Treated Liquor (Bottoms)				
	BOD ppm	COD mg/l	Solids %	Na ppm	pH	BOD ppm	COD mg/l	Solids %	Na ppm	pH	BOD ppm	COD mg/l	Solids %	Na ppm	pH
L_0, G_1, C_0	360	350	0.114	220	9.0	360	480	0.116	220	8.9	340	320	0.111	220	8.9
L_1, G_2, C_0	360	720	0.111	230	8.9	480	800	0.116	230	8.8	220	670	0.105	210	8.8
L_2, G_0, C_0	340	575	0.111	210	9.0	380	945	0.131	220	8.8	300	495	0.120	195	8.9
L_0, G_0, C_1	340	545	0.059	205	8.9	480	990	0.153	215	8.8	300	480	0.103	195	8.9
L_1, G_1, C_1	340	545	0.111	210	8.8	400	670	0.120	225	8.7	320	447	0.105	205	8.8
L_2, G_2, C_1	340	367	0.105	210	8.7	360	400	0.115	220	8.6	320	350	0.108	200	8.6
L_0, G_2, C_2	360	350	0.107	200	8.7	380	545	0.114	215	8.6	360	335	0.112	200	8.6
L_1, G_0, C_2	480	378	0.113	200	8.8	810	610	0.169	215	8.6	360	320	0.111	205	8.8
L_2, G_1, C_2	380	385	0.118	200	8.8	420	510	0.128	220	8.7	340	350	0.121	205	8.7

APPENDIX I-B - (Continued)

TABLE 4
EXPERIMENTAL FOAMING TENDENCY DATA FOR FACTORIAL EXPERIMENTS

Block I				Block II				Block III			
Experimental Conditions	H*, Inches			Experimental Conditions	H*, Inches			Experimental Conditions	H*, Inches		
	Feed	Top	Bottom		Feed	Top	Bottom		Feed	Top	Bottom
L_0, G_0, C_0	37	52	26	L_0, G_0, C_2	52	--	31	L_0, G_1, C_0	37	60	28
L_1, G_1, C_0		48	18	L_1, G_1, C_2		65	38	L_1, G_2, C_0		58	22
L_2, G_2, C_0			16	L_2, G_2, C_2		57	17	L_2, G_0, C_0		--	25
L_0, G_2, C_1	35	56	21	L_0, G_1, C_1	51	--	44	L_0, G_0, C_1		43	25
L_1, G_0, C_1		--	25	L_1, G_2, C_1		60	--	L_1, G_1, C_1		64	17
L_2, G_1, C_1		59	17	L_2, G_0, C_1		56	36	L_2, G_2, C_1		--	17
L_0, G_1, C_2		66	30	L_0, G_2, C_0			25	L_0, G_2, C_2	43	47	30
L_1, G_2, C_2		55	32	L_1, G_0, C_0			--	L_1, G_0, C_2		--	29
L_2, G_0, C_2		55	20	L_2, G_1, C_0			26	L_2, G_1, C_2		--	17

APPENDIX I-B
(Continued)

TABLE 5

EFFECTS OF LIQUID FEED RATE, GAS RATE, AND LIQUID COLUMN HEIGHT ON B.O.D. REDUCTION(1)

Air Rate Levels (SCFM)	Liquid Rate Levels (gpm)	% BOD Reductions for the Column Heights			Mean Value for Each Air Rate(2)	Partial Mean Value for Liquid Rates		
		2 ft	4 ft.	8 ft		0.2 gpm	0.6 gpm	1.0 gpm
0.12	0.2	+ 12	+ 21	+ 14	+ 13	+ 16		
	0.6	+ 29	- 34	+ 52			+ 16	
	1.0	+ 12	+ 16	+ 0				+ 9
0.39	0.2	+ 15	- 21	+ 37	+ 13	+ 10		
	0.6	+ 5	+ 11	+ 21			+ 12	
	1.0	+ 18	+ 17	+ 10				+ 15
0.78	0.2	- 7	+ 11	+ 37	+ 17	+ 14		
	0.6	- 8	+ 19	+ 42			+ 18	
	1.0	+ 15	+ 27	+ 16				+ 19

Mean Experimental Value for Each Column Ht.(3)			Total Mean Value for Each Feed Rate(4)		
+ 10	+ 8	+ 25	+ 13	+ 15	+ 14

(1) Percent BOD Reduction = $100\left[1 - \left(\frac{X_B}{X_F}\right)\left(\frac{B}{F}\right)\right]$. $\left(\frac{X_B}{X_F}\right)$ = Concentration Ratio. $\left(\frac{B}{F}\right)$ = Partition Ratio = 0.95

(2) Equals First Order Effect of Air Rate.
(3) Equals First Order Effect of Column Height.
(4) Equals First Order Effect of Feed Rate.

APPENDIX I-B - (Continued)

TABLE 6

EFFECTS OF LIQUID FEED RATE, GAS RATE, AND LIQUID COLUMN HEIGHT ON C.O.D. REDUCTION(1)

Air Rate Levels (SCFM)	Liquid Rate Levels (gpm)	% COD Reductions for the Column Heights			Mean Value for Each Air Rate(2)	Partial Mean Value for Liquid Rates		
		2 ft	4 ft	8 ft		0.2 gpm	0.6 gpm	1.0 gpm
0.13	0.2	+ 17	+ 24	+ 18		+ 20		
	0.6	+ 20	+ 38	+ 8	+ 19		+ 22	
	1.0	+ 22	+ 16	+ 9				+ 16
0.39	0.2	+ 14	+ 28	+ 5		+ 16		
	0.6	+ 20	+ 18	+ 21	+ 16		+ 20	
	1.0	+ 17	+ 9	+ 9				+ 12
0.78	0.2	+ 5	+ 5	+ 19		+ 10		
	0.6	+ 24	+ 12	+ 11	+ 11		+ 16	
		+ 9	+ 8	+ 9				+ 9
		Mean Experimental Value for Each Column Ht.(3)				Total Mean Value for Each Liquid Rate(4)		
		+ 16	+ 18	+ 12		+ 15	+ 19	+ 12

(1) Percent COD Reduction = $100\left[1 - \frac{(X_B)(B)}{(X_F)(F)}\right]$; $\frac{(X_B)}{(X_F)}$ = Concentration Ratio; $\frac{(B)}{(F)}$ = Partition Ratio = 0.95.

(2) Equals First Order Effect of Air Rate.
(3) Equals First Order Effect of Column Height.
(4) Equals First Order Effect of Feed Rate.

APPENDIX I-B
(Continued)

TABLE 7
EFFECTS OF LIQUID RATE, GAS RATE, AND LIQUID COLUMN HEIGHT ON SOLIDS REDUCTION(1)

Air Rate Levels (SCFM)	Liquid Rate Levels (gpm)	% Solids Reduction for the Column Heights			Mean Value for Each Air Rate(2)	Partial Mean Value for Liquid Rates		
		2 ft	4 ft	8 ft		0.2 gpm	0.6 gpm	1.0 gpm
0.13	0.2	- 14	+ 2	+ 7		- 1.7		
	0.6	+ 1	+ 32	+ 6	- 5		+ 13	
	1.0	- 15	- 75	+ 9				- 27
0.39	0.2	+ 6	+ 19	+ 3		+ 9.3		
	0.6	+ 1	+ 19	+ 6	+ 8		+ 8.7	
	1.0	- 3	+ 3	+ 25				+ 8.3
0.78	0.2	+ 7	+ 2	- 2		+ 2.3		
	0.6	+ 10	- 9	+ 2	+ 3		+ 1	
	1.0	+ 3	+ 10	+ 1				+ 4.7

Mean Experimental Value for Each Column Ht.(3)			Total Mean Value for Each Liquid Rate(4)		
- 1	0	+ 7	3	8	- 5

(1) Percent Solids Reduction = $100\left[1 - \frac{(X_L)(B)}{(X_F)(F)}\right]$; $\frac{(X_B)}{(X_F)}$ = Concentration Ratio; $\frac{(B)}{(F)}$ = Partition Ratio = 0.95.
(2) Equals First Order Effect of Air Rate.
(3) Equals First Order Effect of Column Height.
(4) Equals First Order Effect of Feed Rate.

APPENDIX I-B - (Continued)

TABLE 8

EFFECTS OF LIQUID FEED RATE, GAS RATE, AND LIQUID COLUMN HEIGHT ON FOAMING TENDENCY REDUCTION[1]

Air Rate Levels (SCFM)	Liquid Rate Levels (gpm)	% Foaming Tendency Reduction for the Column Ht. 2 ft	4 ft	8 ft	Mean Value for Each Air Rate[2]	Partial Mean Value for Liquid Rates 0.2 gpm	0.6 gpm	1.0 gpm
0.13	0.2	43	29	32	33	35		
	0.6	32	29	-			31	
	1.0	40	29	30				33
0.39	0.2	60	51	49		53		
	0.6	27	51	51	38		43	
	1.0	14	15	24				18
0.78	0.2	67	51	57		58		
	0.6	9	-	41	43		25	
	1.0	30	40	51				40

Mean Experimental Value for Each Column Ht.[3]			Total Mean Value for Each Feed Rate[4]		
36	37	42	49	33	30

(1) Percent Foaming Tendency Reduction = $100\left[1 - \frac{(X_B)(B)}{(X_F)(F)}\right]$; $\frac{(X_B)}{(X_F)}$ = Ratio of bottom-to-Feed Foaming Tendency

$\frac{(B)}{(F)}$ = Partition Ratio = 0.95; X_F = Average of all measurements in feed.

(2) Equals First Order Effect of Air Rate.
(3) Equals First Order Effect of Column Height.
(4) Equals First Order Effect of Feed Rate.

APPENDIX II

STUDY OF TEMPERATURE EFFECTS WITH STEADY FLOW OPERATION

TABLE 1
EXPERIMENTAL DATA FOR STUDY OF TEMPERATURE EFFECT WITH VARYING LIQUID COLUMN HEIGHT

Column Height (Ft)	Sample	83°F		113°F		143°F	
		B.O.D.	C.O.D.	B.O.D.	C.O.D.	B.O.D.	C.O.D.
2	Feed	480	880				
	Bottom	420	850				
	Top	500	975				
	Feed			180	915		
	Bottom			160	865		
	Top			260	1070		
	Feed					220	880
	Bottom					180	815
	Top					240	1260
4	Feed	460	945				
	Bottom	420	880				
	Top	480	1120				
	Feed			460	865		
	Bottom			420	815		
	Top			480	910		
	Feed					440	865
	Bottom					400	800
	Top					440	990
8	Feed	440	815				
	Bottom	440	735				
	Top	440	975				
	Feed			420	815		
	Bottom			380	783		
	Top			480	910		
	Feed					440	865
	Bottom					420	830
	Top					460	970

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APPENDIX III
STUDY OF EFFECT OF FEED AND REFLUX POSITION AND EFFECT OF USING SHORT LIQUID COLUMNS

TABLE 1
EXPERIMENTAL AND CALCULATED DATA FOR STEADY FLOW OPERATION WITH VARYING FEED AND REFLUX POSITIONS

Position as Height Above Liquid		Experimental BOD Data* (ppm) for			BOD Treatment Concentration Ratios	
Feed	Reflux	Feed	Bottom	Product	$(\frac{\text{BOD of B}}{\text{BOD of F}})$	$(\frac{\text{BOD of P}}{\text{BOD of F}})$
4	4	283	270	300	0.95	1.06
4	8	315	308	325	0.98	1.03
8	0	335	338	445	1.01	1.33
0	0	300	317	383	1.06	1.28

*Conditions: Foam Height = 8 feet; liquid height = 4 feet; $\frac{G}{L} = 1.5$; $\frac{B}{F} = 0.95$. Data were averages of three measurements.

******

TABLE 2
EXPERIMENTAL AND CALCULATED DATA FOR STEADY FLOW OPERATION WITH SHORT LIQUID COLUMN HEIGHTS

Liquid Column Height (Ft.)	Experimental BOD Data* (ppm) for			BOD Treatment Concentration Ratios	
	Feed	Bottoms	Product	$(\frac{\text{BOD of B}}{\text{BOD of F}})$	$(\frac{\text{BOD of P}}{\text{BOD of F}})$
0.5	500	495	535	0.99	1.07
2.5	470	445	533	0.95	1.13
4.5	500	480	555	0.96	1.11
6.5	445	472	523	1.06	1.18

*Conditions: Foam height = 5.5 feet; $\frac{G}{L} = 1.5$, $\frac{B}{F} = 0.95$. Data averaged from four measurements.

APPENDIX III
(Continued)

TABLE 3
B.O.D. DETERMINATIONS FOR VARYING REFLUX RATIOS
IN STEADY FLOW OPERATION

Reflux Ratio	B.O.D. Concentration (ppm) in Feed	Bottom	Top
0	300	284	350
		250	350
		284	384
		317	367
1.6	300	232	310
		250	340
		217	250
		232	390
3.6	324	217	300
		232	318
		232	284
		217	300
4.1	313	300	550
		280	300
		280	330
		330	280
5.2	298	250	350
		250	330
		280	300
		220	320
7.4	322	267	--
		300	--
		284	--
		267	--
16.7	324	250	--
		267	--
		284	--
Infinite	270	300	--
		250	--
		250	--

APPENDIX IV-A
EXPERIMENTAL AND CALCULATED DATA FOR BATCH EXPERIMENTS

TABLE 1
EXPERIMENTAL AND CALCULATED DATA FOR BATCH STUDY OF COLUMN HEIGHT EFFECTS

Experimental Data					Data Req'd. by Equation (7)for Evaluating Enrichment Factor		
Initial Liquid Column Height (ft)	Sparging Time (min)	Liquid Volume in Column (l)	Measured BOD (ppm)	Smoothed BOD Values From Straight Line Best Representing Time Versus BOD (ppm)	Log of BOD (gms) in Column: Measured Points	Log of BOD (gms) in Column: Smoothed Points	Log of Liquid Volume in Column
10	0	65	400	--	4.416	--	1.814
	10	63	370	380	4.368	4.380	1.800
	30	59	380	380	4.352	4.352	1.772
	50	55	380	380	4.320	4.320	1.741
	70	51	380	380	4.288	4.288	1.708
	90	47	380	380	4.252	4.252	1.673
	110	43	380	380	4.214	4.214	1.644
	130	39	380	380	4.172	4.172	1.592
	143	38	385	380	4.160	4.160	1.580
8	0	52.1	430	--	4.352	--	1.718
	5	51.1	390	385	4.300	4.294	1.710
	25	47.1	--	385		4.270	1.674
	55	41.1	380	385	4.194	4.200	1.614
	85	35.1	380	385	4.126	4.132	1.546
	100	31.0	390	385	4.083	4.078	1.492
4	0	26	430	--	4.049	--	1.416
	10	24	390	400	3.972	3.983	1.381
	30	20	420	400	3.925	3.904	1.302
	50	16	400	400	3.807	3.807	1.205
	70	12	380	400	3.682	3.682	1.080
	82	10	420	400	3.622	3.603	1.000

---(Continued)---

TABLE 1 - (Continued)

Experimental Data					Data Req'd. by Equation (7) for Evaluating Enrichment Factor		
					Log of BOD (gms) in Column		
Initial Liquid Column Height (ft)	Sparging Time (min)	Liquid Volume in Column (l)	Measured BOD (ppm)	Smoothed BOD Values From Straight Line Best Representing Time Versus BOD (ppm)	Measured Points	Smoothed Points	Log of Liquid Volume in Column
6	0	39.1	567		4.347		1.593
	17	35.8	535	534	4.283	4.282	1.554
	57	28.0	500	527	4.146	4.170	1.448
	87	22.1	517	522	4.059	4.062	1.345
	117	16.9	517	517	3.942	3.942	1.228
8	0	52.1	568		4.472		1.718
	18	48.3	435	497	4.314	4.378	1.684
	48	42.5	485	486	4.315	4.316	1.629
	78	34.4	517	477	5.251	4.216	1.537
	133	25.5	467	462	4.077	4.072	1.408
	151	22.6	467	460	4.024	4.018	1.354
10	0	65.1	590		4.586		1.816
	20	61.3	568	560	4.542	4.536	1.788
	92	47.1	535	516	4.402	4.388	1.674
	124	40.6	500	497	4.308	4.306	1.610
	154	34.5	467	477	4.208	4.217	1.538
	181	30.4	467	462	4.153	4.148	1.484

APPENDIX IV-A
(Continued)

TABLE 2
EXPERIMENTAL AND CALCULATED DATA FOR BATCH STUDY OF SPARGER POROSITY EFFECTS

Experimental Data					Data Req'd. by Equation (7) for Evaluating Enrichment Factor		
					Log of BOD (gms) in Column		
Average Sparger Porisity (Microns)	Sparging Time (min)	Liquid Volume in Column (l)	Measured BOD (ppm)	Smoothed BOD Values From Straight Line Best Representing Time Versus BOD (ppm)	Measured Points	Smoothed Points	Log of Liquid Volume in Column
25-50	0	52.1	440		4.361		1.718
	5	48.7	480	441	4.371	4.325	1.688
	30	33.7	420	438	4.140	4.170	1.528
	50	27.3	400	433	4.049	4.074	1.437
	65	25.7	440	430	4.054	4.044	1.410
145-175	0	52.1	450		4.372		1.718
	5	50.1	470	448	4.373	4.353	1.700
	20	44.5	420	443	4.272	4.295	1.649
	45	36.6	420	434	4.188	4.201	1.564
	75	33.6	430	422	4.154	4.146	1.520
70-100	0	52.1	450		4.372		1.718
	5	48.1	450	444	4.336	4.330	1.684
	20	36.5	420	428	4.186	4.195	1.563
	40	26.9	400	407	4.032	4.040	1.430
	55	25.5	400	392	4.009	4.000	1.408

APPENDIX IV-A
(Continued)

TABLE 3
EXPERIMENTAL AND CALCULATED DATA FOR BATCH STUDY OF AIR RATE EFFECT

Experimental Data					Data Req'd. by Equation (7) for Evaluating Enrichment Factor		
					Log of BOD (gms) in Column		
Air Rate (SCFM)	Sparging Time (min)	Liquid Volume in Column (l)	Measured BOD (ppm)	Smoothed BOD Values From Straight Line Best Representing Time Versus BOD (ppm)	Measured Points	Smoothed Points	Log of Liquid Volume in Column
0.26	0	52.1	310		4.210		1.718
	5	51.1	320	315	4.206	4.200	1.700
	15	46.1	330	310	4.182	4.156	1.665
	30	41.6	300	302	4.093	4.100	1.620
	45	39.3	280	294	4.052	4.063	1.600
	69	38.6	280	292	4.047	4.040	1.590
0.52	0	52.1	300		4.195		1.718
	10	41.3	320	292	4.122	4.082	1.616
	20	33.5	280	285	3.973	3.981	1.526
	32	30.6	270	276	3.918	3.927	1.486
	43	29.9	270	268	3.908	3.905	1.476
0.78	0	52.1	320		4.223		1.718
	5	43.1	280	310	4.082	4.127	1.636
	15	29.8	320	292	3.980	3.940	1.475
	25	24.0	270	275	3.812	3.820	1.381
	34	22.7	270	259	3.804	3.770	1.357

APPENDIX IV-A
(Continued)

TABLE 4
EXPERIMENTAL AND CALCULATED DATA FOR BATCH STUDY OF FOAM HEIGHT EFFECTS

Experimental Data					Data Req'd. by Equations (7) for Evaluating Enrichment Factor		
					Log of BOD (gms) in Column		
Foam Column Height (ft)	Sparging Time (min)	Liquid Volume in Column (l)	Measured BOD (ppm)	Smoothed BOD Values From Straight Line Best Representing Time Versus BOD (ppm)	Measured Points	Smoothed Points	Log of Liquid Volume in Column
8	0	26	400		4.018		1.416
	5	23.6	425	408	4.002	3.984	1.374
	10	21.7	420	408	3.960	3.948	1.337
	15	20.6	400	408	3.917	3.926	1.314
	20	20.1	420	408	3.926	3.914	1.304
	23	20.0	390	408	3.892	3.912	1.302
4	0	26.0	380		4.018		1.416
	5	23.3	410	392	3.918	3.961	1.368
	10	21.1	400	392	3.926	3.918	1.325
	15	19.6	380	392	3.872	3.886	1.292
	25	19.2	400	392	3.886	3.877	1.284
2	0	26.0	400		4.018		1.416
	5	23.1	380	389	3.985	3.954	1.364
	10	20.8	350	388	3.908	3.908	1.319
	15	19.3	370	387	3.874	3.874	1.286
	26	18.8	400	386	3.877	3.862	1.275

APPENDIX IV-A
(Continued)

TABLE 5
EXPERIMENTAL AND CALCULATED DATA FOR BATCH STUDY OF MILL EFFLUENT TRIBUTARY STREAMS

Experimental Data					Data Req'd. by Equation (7) for Evaluating Enrichment Factor		
					Log of BOD (gms) in Column		
Stream	Sparging Time (min)	Liquid Volume in Column (l)	Measured Points (ppm)	Smoothed BOD Values From Straight Line Best Representing Time Versus BOD (ppm)	Measured Points	Smoothed Points	Log of Liquid Volume in Column
6th Effect Condensate	0	52.1	840	850	4.648		1.718
	5	48.1	880	850	4.628	4.612	1.683
	10	44.3	870	850	4.587	4.577	1.649
	20	37.1	820	850	4.484	4.500	1.570
	30	30.9	840	850	4.415	4.420	1.491
	45	23.7	840	850	4.300	4.306	1.376
6th Effect Condensate	0	52.1	940		4.691		1.718
	5	48.1	870	825	4.622	4.600	1.683
	20	44.6	820	825	4.564	4.567	1.650
	25	42.9	800	825	4.536	4.549	1.633
	40	38.0	800	825	4.484	4.497	1.580
	50	35.2	820	825	4.461	4.464	1.547
	60	32.9	820	825	4.432	4.436	1.518
	75	30.7	845	825	4.415	4.404	1.488

--Continued--

TABLE 5
(Continued)

Stream	Sparging Time (min)	Liquid Volume in Column (l)	Measured Points (ppm)	Smoothed BOD Values From Straight Line Best Representing Time Versus BOD (ppm)	Data Req'd. by Equation (7) for Evaluating Enrichment Factor: Log of BOD (gms) in Column, Measured Points	Log of BOD (gms) in Column, Smoothed Points	Log of Liquid Volume in Column
Small Flume	0	52.1	750		4.593		1.718
	7	50.7	675	665	4.535	4.529	1.706
	20	48.1	650	661	4.496	4.504	1.684
	45	43.1	700	652	4.481	4.450	1.635
	60	40.1	650	647	4.417	4.415	1.604
	70	38.1	700	644	4.426	4.390	1.582
	85	35.1	600	638	4.324	4.351	1.546
	94	33.5	625	635	4.328	4.329	1.526
Large Flume	0	52.1	600		4.496		1.718
	5	51.1	600	600	4.488	4.488	1.710
	15	49.1	600	600	4.470	4.470	1.692
	30	46.1	600	600	4.443	4.443	1.665
	45	43.1	600	600	4.414	4.414	1.636
	60	40.1	650	600	4.417	4.382	1.604
	90	34.1	650	600	4.346	4.312	1.534
	100	32.1	600	600	4.286	4.286	1.507
	129	26.7	550	600	4.168	4.206	1.427

APPENDIX IV-A
(Continued)

TABLE 6
EXPERIMENTAL AND CALCULATED DATA FOR BATCH STUDY OF TEMPERATURE EFFECTS

Experimental Data					Data Req'd. by Equation (7) for Evaluating Enrichment Factor		
					Log of BOD (gms) in Column		
Temperature (°F)	Sparging Time (min)	Liquid Volume in Column (l)	Measured Points (ppm)	Smoothed BOD Values from Straight Line Best Representing Time Versus BOD (ppm)	Measured Points	Smoothed Points	Log of Liquid Volume in Column
136°	0	52.1	480		4.400		1.718
	5	51.1	470	465	4.382	4.377	1.710
	20	48.1	450	455	4.336	4.341	1.684
	50	42.1	450	434	4.279	4.263	1.626
	62	40.8	415	426	4.230	4.238	1.606
110°	0	52.1	450		4.371		1.718
	5	51.1	450	444	4.363	4.357	1.710
	25	47.1	420	433	4.298	4.312	1.674
	45	43.1	380	422	4.216	4.260	1.636
	68	39.0	430	407	4.225	4.201	1.592
	81	37.0	400	400	4.171	4.171	1.569
83°	0	52.1	450		4.371		1.718
	5	51.1	435	440	4.348	4.354	1.710
	25	47.1	450	429	4.328	4.306	1.674
	55	41.1	430	412	4.248	4.230	1.615
	70	38.1	380	403	4.162	4.187	1.582
	90	34.1	400	392	4.136	4.127	1.534
	107	31.8	375	362	4.077	4.062	1.503

APPENDIX IV-A

TABLE 7

EXPERIMENTAL AND CALCULATED DATA FOR BATCH STUDY OF ADJUSTED pH EFFECTS

Experimental Data					Data Req'd. by Equation (7) for Evaluating Enrichment Factor		
					Log of BOD (gms) in Column		
pH	Sparging Time	Liquid Volume in Column	Measured Points	Smoothed BOD Values from Straight Line Best Representing Time Versus BOD	Measured Points	Smoothed Points	Log of Liquid Volume in Column
	(min)	(l)	(ppm)				
10.0	0	52.1	600		4.496		1.718
	15	40.1	640	617	4.411	4.394	1.604
	25	32.3	600	607	4.288	4.293	1.510
	35	26.5	640	598	4.230	4.201	1.424
	45	22.9	585	589	4.128	4.130	1.360
	57	19.7	550	578	4.036	4.057	1.295
8.3	0	52.1	530		4.432		1.718
	15	40.4	455	506	4.265	4.312	1.606
	25	33.5	450	492	4.179	4.218	1.526
	35	29.4	540	478	4.201	4.148	1.469
	47	27.5	475	461	4.117	4.104	1.430
7.0	0	52.1	500		4.417		1.718
	10	44.0	480	483	4.326	4.328	1.644
	20	37.5	470	465	4.247	4.242	1.575
	31	34.5	450	447	4.192	4.189	1.538
	35	34.1	430	439	4.166	4.176	1.534
5.8	0	52.1	450		4.371		1.718
	11	45.5	430	432	4.292	4.294	1.659
	20	40.9	420	427	4.235	4.242	1.612
	35	38.8	430	419	4.223	4.212	1.590
3.8	0	52.1	370		4.286		1.718
	11	51.7	425	420	4.343	4.338	1.714
	20	51.5	410	420	4.325	4.336	1.712
	25	51.4	430	420	4.344	4.334	1.711

APPENDIX IV-B
BOD TREATMENT AS EVALUATED FROM BATCH EXPERIMENTS

TABLE 1
ENRICHMENT FACTORS AND BOD DISCONTINUITY DATA FOR BATCH EXPERIMENTS

Experimental Variables and Their Magnitudes	Enrichment Factor	Discontinuity at Time Zero
Column Height		
4 feet	1.01	8.3
8 feet	1.00	5.0
10 feet	1.02	9.5
6 feet	1.04	-7.2
8 feet	1.11	12.6
10 feet	1.32	1.7
Temperature		
83°F	1.22	3.2
110	1.34	1.1
136	1.44	-2.1
Sparger Porosity		
20-50 microns	1.13	0
75-100	1.10	0
145-175	1.04	1.8
Air Rate		
0.26 SCFM	1.36	-2.6
0.52	1.12	0
0.78	1.15	0
Foam Height		
2 feet	1.00	0
8	1.00	0
Effect of Different Feed Streams		
Pulp Mill Effluent	1.12	0
Paper Mill Effluent	1.01	12
6th Effect Condensate	1.00	6
Acidification (Effect of pH)		
3.8	1.00	-12.5
5.8	1.11	2.7
7.0	1.22	0
8.3	1.19	0.4
10.0	1.06	5.0

APPENDIX V
ANALYTICAL DATA

TABLE 1
ANALYSIS OF FEED, TREATED LIQUID, AND PRODUCT IN FLOW EXPERIMENTS

	Composition of Each Stream as Weight, %											
	Feed				Treated Liquid				Foamed Product			
Experiment	Total Solids	Ash	Tall Oil	All Other Organics	Total Solids	Ash	Tall Oil	All Other Organics	Total Solids	Ash	Tall Oil	All Other Organics
1	0.143	0.122	0.003	0.018	0.132	0.111	0.003	0.018	0.133	0.110	0.005	0.018
2	0.216	0.100	0.005	0.111	0.212	0.099	0.005	0.108	0.231	0.110	0.005	0.116
3	0.215	0.101	0.005	0.111	0.213	0.098	0.005	0.110	0.220	0.103	0.006	0.111
4	0.227	0.108	0.004	0.115	0.222	0.106	0.002	0.114	0.246	0.107	0.004	0.135
5	0.226	0.103	0.004	0.119	0.220	0.104	0.003	0.113	0.232	0.103	0.005	0.124
6	0.160	0.068			0.128	0.054	0.005	0.069	0.134	0.056	0.006	0.072
7	0.163	0.068			0.132	0.054	0.005	0.073	0.141	0.058	0.006	0.077
8	0.162	0.064	0.006	0.062	0.130	0.054	0.004	0.071	0.134	0.059	0.006	0.069
9	0.158	0.077	0.002	0.079	0.142	0.076	0.001	0.065				
10	0.150	0.075	0.002	0.074	0.143	0.073	0.000	0.070				
11	0.161	0.074	0.003	0.084	0.148	0.071	0.001	0.076				
12	0.153	0.085	0.002	0.066	0.153	0.088	0.002	0.061	0.155	0.084	0.004	0.067
13	0.159	0.086	0.002	0.071	0.152	0.085	0.002	0.065	0.162	0.087	0.004	0.071

APPENDIX V
ANALYTICAL DATA

TABLE 2
TALL OIL ANALYSES IN BATCH EXPERIMENTS

Sample	Weight Per Cent Tall Oil in Experiments					
	I	II	III	IV	V	VI
Feed Liquid	0.005	0.006	0.005	0.005	0.004	0.004
Foamate After Sparging for:						
5 minutes		0.020		0.007	0.011	0.009
10	0.005					
22	0.006					
25			0.005	0.005		
30					0.007	0.007
35		0.016				
50					0.004	
60						0.004
64	0.008					
65			0.004			0.005
80		0.004				
100					0.004	
102						0.005
Remaining Column Liquid	0.001	0.003	0.002	0.000	0.002	

Conditions: Initial 8 ft. liquid column and 4 ft. foam height, 0.26 SCFM Air Rate; room temperature.

APPENDIX V
(Continued)

TABLE 3
ANALYSES OF STREAMS TAKEN FROM KRANNERT DIVISION WASTE TREATMENT PLANT

Sample	Constituents as Weight Per Cent of Sample			
	Total Solids	Ash	Tall Oil	All Organics Other Than Tall Oil
Primary Clarifier Effluent	0.125 Avg. Value from 78 measurements with range 0.100 to 0.180	0.078 Avg. Value from 9 measurements with range 0.045 to 0.108	0.004 Avg. Value from 9 measurements with range 0.002 to 0.005	0.000 Avg. Value from 0.084 measurements with range 0.066 to 0.119
Pulp Mill Effluent	0.160	0.068	--	--
	0.163	0.068	--	--
	0.162	0.064	0.006	0.062
Paper Mill Effluent Plus Decker Filtrate	0.158	0.077	0.002	0.079
	0.150	0.075	0.001	0.074
	0.161	0.074	0.003	0.084
Dense Foam From Primary Clarifier	0.64	--	0.186	--
Dense Foam From Secondary Clarifier	2.32	0.54	0.158	1.62

1 Accession Number: W70-03350

2 Subject Field & Group: 05D, 05G

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

5 Organization

Georgia Kraft Company, Rome, Georgia, Research and Development Center

6 Title

FOAM SEPARATION OF KRAFT PULPING WASTES

10 Author(s)

16 Project Designation

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25 Identifiers (Starred First)

27 Abstract

Laboratory studies of foam separation were conducted to determine the feasibility of this process for reducing B.O.D., solids content, and foaming tendency of clarified kraft mill effluent. Since kraft pulping wastes have a natural tendency to foam, it was expected that the foaming process, which has been found to be useful in treating domestic wastes, might have applications in treatment of these effluents.

Both continuous flow and batch experiments were conducted, and liquid and foam heights, liquid feed rates, air sparging rates, and temperature were varied over wide ranges.

The B.O.D. reduction in the treated liquid was disappointingly small, averaging less than 5 per cent, and the B.O.D. enrichment in the foam phase was in most cases less than 1.5 times that of the feed. Solids removal was correspondingly low.

Foaming tendency, however, was significantly reduced by the intentional foaming process with reductions of 40 to 60 per cent in this variable being obtained. The reduction in foaming tendency was a strong function of gas-to-liquid ratio with the most effective operating range being between 1.0 and 1.5 SCFM/gallon.